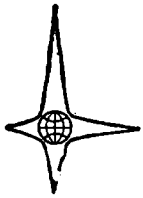
V. V. SUSHKOV

TECHNICAL THERMO DYNAMICS



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Prof. V. SUSHKOV

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EDITOR'S PREFACE TO THE RUSSIAN EDITION

Professor Sushkov's *Technical Thermodynamics* was compiled mainly for students of technical colleges that do not specialise in power engineering. On account of its happy combination of clarity and brevity it has become the most widely used of the many books on this subject published in recent years.

Five editions of the book have been sold out, and this, the sixth edition, not only preserves all the virtues of previous editions but has been brought up to date in accordance with the latest curricula approved by the Ministry of Higher Education of the U.S.S.R.

In view of the fact that an understanding of the physical fundamentals of the subject is important from any point of view, and also because considerable and well-deserved attention has been paid in recent years to what is known as the entropic method of defining power losses, this edition also contains the two chapters which I added to the fifth edition: "Entropy and Probability" (5-13) and "Reversibility and the Performance of Work" (5-14). Further additions and amendments that have been made reflect the development of science and engineering in the years that have elapsed since the fifth edition was published. The Introduction, in particular, has been extended to include the development of Soviet power engineering for the next few years; the range of the thermodynamic tables for water and steam has been extended and some corrections have been made.

V. Kirillin

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Introduction

1. The Subject of Thermodynamics. The degree to which a body is heated or, more broadly, the thermal state of a body, depends to a considerable extent on the amount of internal or heat energy possessed by the body, the term "body" being understood as any gaseous, liquid or solid substance. Heat energy is the sum of the kinetic energy and potential energy of the molecules, atoms and other elementary particles of a body. Since any form of energy may be converted into any other, it follows that heat energy, as a particular case, can be converted into mechanical energy, or work, and vice versa. Modern power engineering is based largely on the conversion of heat into mechanical work, which, in turn, is usually turned into electricity at power plants, since electricity is the form of energy best adapted to transmission over long distances. The heat required for this process may be obtained from the combustion of some type of fuel in a steam boiler, or by its combustion directly in an internal combustion engine; in the latter case the chemical energy of the fuel is converted into heat.

Electric power generation plays an extremely important role in the development of the Soviet economy. The Seven-Year Plan for the Development of the Soviet Economy (1959-1965) gives a prominent place to the building of new power plants and to raising the technical efficiency of production. Suffice it to say that while the country's power output increased from 1,900 million kwh to 233,000 million kwh between 1913 and 1958, during the seven years 1959-1965 it will increase to between 500,000 and 520,000 million kwh, i. e., to more than double the 1958 figure.

Steam power plants have always been basic in Soviet power engineering and will continue to hold a leading place

under the seven-year plan, plants using all types of fuel being envisaged. Since steam power plants can be built at low cost and in a short time, they permit of a rapid rate of development. Some very big steam power plants are to be built under the plan, many of them over a million kilowatts capacity.

Atomic power stations, using the nuclear energy of certain isotopes of uranium and plutonium for the production of electric power have recently come in for more extensive development. Production costs at atomic power stations are being gradually reduced and it may be assumed that in the near future atomic power stations will be built on a scale similar to that of steam power plants.

The problem of constructing thermonuclear power plants which, it will be remembered, was initiated by the Soviet Union, is of great interest. The work now being done in this field is connected primarily with the problem of regulating the thermonuclear reaction. The use of this reaction would provide practically unlimited resources for the production of electric power.

The energy of rivers, or water power, is also an important source of energy, but today it still plays a less significant role than steam power engineering.

Water energy has some important advantages—first, power produced at hydroelectric stations is cheaper than that of steam power plants; secondly, the source of energy is constantly being renewed. It is, therefore, economically important to make greater use of water power. With the exception of small water-mills, the energy of rivers was little employed in pre-revolutionary Russia, and this despite the fact that the reserves of water energy (over 300,000,000 kw) are the greatest in the world. After the October Revolution the employment of water resources in power engineering assumed the proper proportions.

The U.S.S.R. has some important achievements in the building of hydroelectric power stations to record; power engineers have completed the building of one of the world's biggest power stations on the Volga and are now working on the Bratsk Power Station on the River Angara, the capacity of which will be 4,500,000 kw when completed. The greater part of this capacity will be made available to industry by 1966.

The rational organisation of the conversion of heat into

mechanical energy is of extreme importance since it lowers the cost of the power produced and economises fuel.

A study of thermal processes, in particular of the conversion of heat into mechanical energy, or work, and the determination of the most favourable conditions for that conversion is the purpose of *technical thermodynamics*, a subject that provides the theoretical basis for a number of special courses such as: steam boiler design, steam turbine design, internal combustion engine design, etc.

2. The Role of Russian and Soviet Scientists in the Development of Technical Thermodynamics. Technical thermodynamics took shape as an independent scientific discipline in the fifties of the nineteenth century when it was called *the mechanical theory of heat*. The basic premises for this branch of science were elaborated a hundred years earlier by the Russian scientist Mikhail Lomonosov, whose writings categorically rejected the theory of *thermogen*, generally accepted in his day, which regarded heat as a weightless substance that could be transmitted from one body to another.

Lomonosov outlined his basic views in a dissertation, *Some Reflections on the Causes of Heat and Cold* (1744-1747), and in his *An Essay on the Theory of the Resilient Power of Air* (1745) and *A Discourse on the Solidity and Liquidity of Bodies* (1760). He maintained that "heat consists of movement within a substance", particularly "of the rotatory motion of the particles of the body, so that the action of the heat originates from the rotatory motion of its particles"; "hot air imparts warmth to an object which it surrounds because its atoms impart rotatory motion to the particles of the body with which it is in contact, and this motion constitutes heat". Although Lomonosov's kinetic theory of heat does not fully coincide with that accepted today, he was a hundred years ahead of West-European scientific thought. Lomonosov was also the first to formulate the law of conservation of matter and energy. His views, however, were not accepted by other scientists of his day and a whole century passed before they became a special branch of learning, the mechanical theory of heat, from which modern technical thermodynamics developed. Lomonosov, therefore, is the father of thermodynamics.

As we have said, the rapid development of technical thermodynamics began in the latter half of the nineteenth cen-

tury. A number of Russian scientists worked in this field; in 1862, Professor M. V. Okatov of St. Petersburg University published his *Proof of the Second Fundamental Theorem of the Theory of Heat as Motion in Its General Form* and in 1871 his course of lectures entitled *Thermostatics, or the First Part of the Mechanical Theory of Heat* (the first Russian printed course of lectures in this subject), that aroused considerable interest both among Russian and foreign scientists; Professor I. A. Vyshnegradsky's papers on the kinetic theory of gases and the mechanical theory of heat appeared in 1876; these papers attracted the attention of the Paris Academy. In 1861, the great Russian chemist, Dmitry Mendeleyev, established the fact that there exists a critical temperature for all liquids. He called it the "absolute boiling point", the highest temperature at which liquids remain in their fluid state, and elaborated the theory of the continuity of the fluid and gaseous states of a substance. A number of other Russian scientists, as well as Mendeleyev, worked on this problem of the critical state of matter; the theoretical and experimental work done by Professors Avenarius, Golitsyn, Stoletov, Nadezhdin, Bogayevsky and Zhuk between 1870 and 1890 became widely known. Some important investigations in the sphere of the kinetic theory of gases were published in the *Journal of the Russian Physico-Chemical Society* between 1885 and 1890 by Professor N. N. Pirogov of Kiev University. The same journal (1880-1900) also published outstanding papers on the analysis of the basic postulates of thermodynamics by N. K. Schiller, another Kiev University professor. An important contribution to the thermodynamics of vapours was made by Professor A. A. Radzig, Corresponding Member of the Academy of Sciences of the U.S.S.R., one of the founders of the theory of steam turbines.

A number of research institutes established since the Great October Socialist Revolution to meet the needs of Soviet industry are working in the fields of heat engineering and theoretical thermodynamics.

In the Soviet years many theoretical and experimental works have appeared. The scientists of the Krzhizhanovsky Institute of Power Engineering, the Dzerzhinsky All-Union Institute of Heat Engineering, the Polzunov Central Turbine and Boiler Institute and several others have carried out some important experiments. Of equal importance is the work

that has been done in Soviet higher educational establishments, among them, Moscow State University, Moscow Institute of Power Engineering and the Baumann Higher Technical School. In particular, great advance has been made in the study of the heat properties of water and water vapours under high pressure and at high temperatures.

A number of excellent textbooks and handbooks on thermodynamics have been issued in very large editions during the Soviet years. Prominent among them is A. S. Yastrzhembsky's textbook that has seen many editions.

Chapter One

GASES. THE BASIC GAS LAWS

1-1. The Basic Constants of the State of a Body. In order to obtain work (mechanical energy) from heat we must have a "*working*" body, through the medium of which we effect the process of converting heat, usually imparted to the body from an outside source, into work. The body changes its state as a result of heat being imparted to it; this state is described by three parameters—*specific pressure, specific volume and temperature.*

Specific pressure. Pressure is brought to bear on the surface of any body by the surrounding medium. At every point on the surface this pressure is exerted perpendicular to the surface of the body towards its centre; equilibrium is effected by an equal pressure exerted by the body on the surrounding medium (the resilience of the body). The *specific pressure, p,* is the pressure per unit of surface and is one of the characteristics or parameters of the body; in thermodynamics the unit of surface area is the square metre, and the pressure is measured in kilograms per square metre (ksm). As this unit is too small for practical use engineers measure pressure in kilograms per square centimetre (kscm); the unit of one kilogram per square centimetre is known loosely as an *atmosphere* and more precisely as a *technical* or *manometric* atmosphere (atm). Therefore,

$$1 \text{ atm} = 1 \text{ kscm} = 10{,}000 \text{ ksm}.$$

In physics an atmosphere is the average pressure of atmospheric air at sea-level, which is 760 mm of a mercury column at 0° C (760 mm Hg). This is known as an *absolute* or *barometric* atmosphere (ata). To express this absolute atmosphere in the engineer's unit of kscm we must first determine the weight of a column of mercury with a cross-section of 1 sq

m and a height of 760 mm; given that a cubic decimetre of mercury at 0° C weighs 13.595 kg, we get

$$1 \text{ ata} = 13.595 \times 100 \times 7.6 = 10{,}332 \text{ ksm} = 1.0332 \text{ atm},$$

i. e., an absolute atmosphere is somewhat larger than a technical atmosphere (3.32% larger).

Any specific pressure is the equivalent of a column of mercury or water of a height sufficient to effect the same pressure on its base; therefore, pressure may be, and usually is, determined by the height of a mercury or water column. According to our definition of a physical atmosphere,

$$1 \text{ ata} = 760 \text{ mm Hg (at } 0^\circ \text{ C)}.$$

therefore,

$$1 \text{ atm} = 1 \text{ kscm} = \frac{760}{1.0332} = 735.6 \text{ mm Hg (at } 0^\circ \text{ C)}.$$

Since mercury expands as temperature increases the height of the mercury column indicating a given pressure will be somewhat greater; this must be taken into consideration when converting the readings of a mercury barometer—the instrument showing the pressure of atmospheric air—into kscm. This is most easily done by reducing the barometer reading to 0° C, using the equation* (which takes into consideration the changes in the specific volume of mercury due to changes in temperature)

$$B_0 = B(1 - 0.000172\,t), \qquad (1\text{-}1)$$

where B—the actual height of the mercury column of the barometer at t° C;

B_0—the barometer reading reduced to 0° C.

In this case the specific pressure of the air is

$$p = \frac{B_0}{735.6} \text{ [kscm]},$$

B_0 being expressed in mm Hg.

In practice very low pressures are sometimes determined by the height of a water column; this is convenient because the height of the water column is 13.595 times greater than that of the mercury column for any given pressure, i. e.,

$$1 \text{ mm Hg} = 13.595 \text{ mm } H_2O.$$

---

* Equation 1-1 is not corrected for the coefficient of expansion of the glass which can be ignored at low temperatures.

Therefore, 1 ata = 760 mm Hg = 13.595 × 760 = = 10,332 mm H_2O = 10.332 m H_2O; 1 atm = 10 m H_2O and, consequently,

$$1 \text{ mm } H_2O = 0.0001 \text{ atm} = 1 \text{ ksm}.$$

Strictly speaking, this relation is only good for water at 4° C; since however, the water column is used to measure only very low pressures the temperature correction is of no significance and is not normally applied.

In engineering, low pressures are mostly measured by a manometer, the spring instrument shown schematically in Fig. 1-1; a spiral tube, one end of which (left) is sealed, has its other end fixed to the housing of the instrument so that it can make contact with the fluid or gas whose pressure p is to be measured. This specific pressure acts on the inner surface of the tube, while the specific pressure p_a, that of the air in the premises (i. e., the barometric pressure), acts on its outer surface.

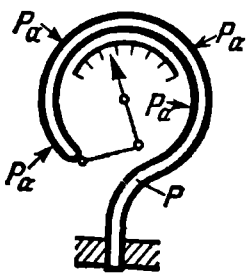


Fig. 1-1

Experiments have shown that if a tube with an elliptical cross-section is used, the greater the difference between the internal and external pressures, the greater the extent to which it opens up (straightens). A pointer indicating the pressure is linked to the free end of the tube—the chief component of the manometer—by a special mechanism.

The free end of the tube changes its position as the internal pressure changes, the pointer moving with it.

This type of manometer, or pressure gauge, is used to measure pressures higher than that of the atmosphere; it indicates a pressure magnitude

$$p_m = p - p_a, \tag{1-2}$$

i. e., the excess of the actual pressure p over that of the atmosphere p_a; in view of this, pressure p_m is called the excess or manometric pressure and p the absolute pressure. We shall designate these atmospheric pressures *atm* for manometric and *ata* for absolute pressure, the unit of measurement being the same in both cases (1 atm = 1 kscm). Manometers are usually designed with a scale showing kscm.

It follows from equation 1-2 that

$$p = p_m + p_a, \tag{1-3}$$

that is, the simultaneous readings of the barometer and the manometer must be added to determine the absolute pressure.

To measure pressures below that of the atmosphere (i. e., the degree of vacuum) a *vacuum gauge* is used; the reading of this instrument gives a unit of pressure

$$p_v = p_a - p, \tag{1-4}$$

that is, the excess of the atmospheric pressure p_a over the absolute pressure p, which is called the vacuum. From equation 1-4 it follows that

$$p = p_a - p_v, \tag{1-5}$$

i. e., to determine the absolute pressure in this case we must know the readings of the vacuum gauge and the barometer taken simultaneously and calculate the former from the latter; obviously, the greater the vacuum gauge reading, the lower the absolute pressure p. Spring vacuum gauges usually give readings in centimetres of the mercury column at 0° C; naturally no correction for temperature is necessary for these readings.

From what has been said it follows that the readings of spring manometers and vacuum gauges depend on barometric pressure, which is variable and depends on time and location. It is clear that the absolute pressure p, and not the manometer reading p_m or the vacuum gauge reading p_v, is the parameter indicating the state of a body.

Specific volume. The second basic magnitude indicating the state of a body is its *specific volume*, v, which is the volume of a unit weight expressed in cubic metres per kilogram (cum-kg). If V is the volume (in cum) of a body weighing G (kg), then

$$v = \frac{V}{G} \text{ cum-kg}. \tag{1-6}$$

The magnitude inverse to the specific volume is the *specific weight*, γ, and

$$\gamma = \frac{1}{v} = \frac{G}{V} \text{ kg-cum}, \tag{1-7}$$

that is, the weight of a unit of volume, or the weight in kilograms of one cubic metre of the substance. Tables of the specific weights of solid and fluid bodies are usually given in kilograms per cubic dacimetre (kcdm) or grammes per cubic centimetre (gccm), the figures being identical in both cases; to convert the figures from the table into kcm they must be multiplied by 1,000. The specific weight of water (at 4° C) is usually taken as unity, since one litre of water weighs one kilogram and one cubic centimetre weighs one gramme; the specific weight of water at 4° C, therefore, is 1,000 kcm.

From equation 1-7 it follows that

$$\gamma v = 1$$

and also that

$$V = Gv = \frac{G}{\gamma} \text{ and } G = \gamma V = \frac{V}{v}.$$

Thus, specific volume and specific weight are mutually dependent so that either of them may serve as an indication of the state of a body.

Temperature. The third basic magnitude indicating the state of a body is its *temperature.* Engineers measure temperature by the international centigrade scale (° C) according to which 0° is the temperature of melting ice and 100° is the temperature at which water boils at sea-level (i. e., at a pressure of 760 mm Hg, or one atmosphere). For thermodynamic investigations the absolute scale is more convenient; this scale is divided in the same way as the centigrade scale but absolute zero is 273 degrees below the melting point of ice. Lomonosov defined absolute zero as "the highest and final degree of cold". The temperature shown on this scale is called *absolute temperature* (T) and is expressed in degrees of the Kelvin scale (° K), readings being 273 degrees greater than those of the ordinary centigrade scale on which zero is taken as the melting point of ice (t° C), i. e.,

$$T = t + 273, \qquad (1\text{-}8)$$

the degrees, as we have said, being the same size on both scales. In particular, equation 1-8 gives us the following basic measurements:

$$0° \text{ K} = -273° \text{ C};\ 0° \text{ C} = 273° \text{ K};\ 100° \text{ C} = 373° \text{ K}.$$

Example 1-1. The manometer of a steam boiler reads 8 kscm. What is the absolute pressure of the steam in the boiler if the mercury barometer shows 700 mm Hg at 25° C in the building?

The barometric pressure reduced to 0° C (equation 1-1) is

$$B_0 = 700\,(1 - 0.000172 \times 25) = 697 \text{ mm Hg};$$

therefore, by equation 1-3,

$$p = 8 + \frac{697}{735.6} = 8.947 \text{ ata}.$$

Example 1-2. The vacuum gauge on the condenser of a steam engine reads 62.5 cm Hg. Find the absolute pressure if the mercury barometer shows 74 cm Hg at a temperature 20° C in the building.

The barometric pressure reduced to 0° C (equation 1-1) is

$$B_0 = 740\,(1 - 0.000172 \times 20) = 737 \text{ mm Hg};$$

by equation 1-5 we get

$$p = 737 - 625 = 112 \text{ mm Hg} = \frac{112}{735.6} = 0.152 \text{ ata}.$$

If the barometric pressure drops to, say, 65 cm Hg and the pressure in the condenser is constant, the vacuum gauge will also give a lower reading. The new barometer reading, reduced to 0° C, will be

$$B_0' = 650\,(1 - 0.000172 \times 20) = 648 \text{ mm Hg},$$

and the new vacuum gauge reading, applying equation 1-4, will be

$$p_v' = 648 - 112 = 536 \text{ mm} = 53.6 \text{ cm Hg},$$

instead of the former 62.5 cm. Thus we see that changes in atmospheric pressure greatly influence vacuum gauge readings; they have practically no effect on manometer readings because the pressure of the air outside the boiler is insignificant in comparison with that being measured by the manometer.

1-2. The Nature of Heat Energy. We know from physics that all matter consists of tiny particles, molecules and atoms, that are in a state of constant motion and are linked to one another by the forces of mutual attraction. Molecular attraction decreases rapidly as the distance between the molecules increases, so that it is only felt at extremely small distances. Molecular attraction is so great in solid bodies that it maintains the moving atoms in a sort of "mean" position about which they oscillate. In gases and superheated vapours the forces of molecular attraction are so small that the molecules, practically speaking, are in free motion and move in straight lines in all directions; this explains why bodies of this kind always strive to fill the volume within which they are confined. The movement of the molecules

in fluids is relatively more restricted than that of gas molecules and the molecules do not move in straight lines but along intricate trajectories determined by the attraction of neighbouring molecules.

According to the postulates of the molecular kinetic theory, heat energy is the kinetic and potential energy of molecules, atoms and other elementary particles. We perceive an acceleration of molecular motion as an increase in the temperature of the body, which, conversely, indicates the intensity of molecular motion.

1-3. The Ideal Gas. The Kinetic Theory of Gases. At the present time the molecular-kinetic theory has been most profoundly and precisely elaborated in its application to gases because these have properties that are simpler than those of solids and fluids. Particularly simple relations are obtained with "*ideal*" or perfect gases, those that consist of fully resilient molecules between which there is no molecular attraction and the volume occupied by them is infinitely small as compared with the volume of the intermolecular space, i. e., the molecules are points of matter.

Molecules are in a state of uninterrupted chaotic motion and their number is tremendous even in a small volume. Given these premises the motion of each molecule, in the absence of external forces, will be in a straight line and regular until it collides with another molecule or with the walls of the vessel. The collisions of molecules against the walls follow rapidly one after another and determine the pressure exerted by the gas on the walls. This pressure is distributed evenly over the walls of the vessels and is everywhere perpendicular to the elements of those walls. Therefore, the pressure per unit of surface area—the specific pressure p—is identical in all directions. This identical pressure is due to the chaotic movements of the molecules, the fact that they move in every possible direction, none having any particular advantage over the others, and the tremendous number of molecules in even a small volume.

According to the laws of physics, the kinetic theory of gases in particular, the magnitude of the specific pressure of an ideal gas on the walls of a vessel is

$$p = \frac{nmw^2}{3}, \qquad (1\text{-}9)$$

where p—the absolute pressure of the gas;

n—the number of molecules in a unit of volume;

m—the mass of a molecule, identical for all molecules in a homogeneous gas;

w—the *square of the mean velocity* of the translational motion of the molecules.

The velocity of the translational motion of individual molecules in a gas at a given state varies; formula 1-9 contains the square of the mean velocity w:

$$w = \sqrt{\frac{w_1^2 + w_2^2 + \ldots + w_n^2}{n}}. \qquad (1\text{-}10)$$

Equation 1-9 is basic to the kinetic theory of gases; if we write it as follows:

$$p = \frac{2}{3} n \frac{mw^2}{2}, \qquad (1\text{-}11)$$

it may be formulated as: *the specific pressure of a gas is numerically equal to two-thirds of the kinetic energy of the translational motion of the molecules contained in one unit of volume.*

If we multiply equation 1-11 by V, the volume of the gas, we get

$$pV = \frac{2}{3} nV \frac{mw^2}{2} = \frac{2}{3} N \frac{mw^2}{2}, \qquad (1\text{-}12)$$

where

$$N = nV,$$

i. e., the number of molecules in the given volume of gas.

The basic postulate of the kinetic theory tells us that the mean kinetic energy of a molecule of gas, $\frac{mw^2}{2}$, is directly related to the absolute temperature T, to which it is directly proportional, i. e.,

$$\frac{mw^2}{2} = aT, \qquad (1\text{-}13)$$

where a—the coefficient of proportionality identical for all gases.

The absolute temperature, therefore, is a measure of the kinetic energy of the translational motion of molecules. The value $T=0°$ K is the equivalent of $w=0$ (equation 1-13); in other words, there is no heat movement of molecules at absolute zero. Obviously there cannot be any value $T<0$.

1-4. The Basic Gas Laws. *The Boyle-Mariotte law.* Taking $\frac{mw^2}{2}=aT$ (equation 1-13) and substituting in equation 1-12, we get,

$$pV=\frac{2}{3}NaT. \tag{1-14}$$

Since a is a constant and for a given mass of gas, N is also constant, when $T=\text{const}$, pV must also be constant, i. e.,

$$\underline{pV=\text{const}} \tag{1-15}$$

so that for 1 kg of gas

$$\boxed{pv=\text{const.}} \tag{1-16}$$

This important conclusion from one of the basic postulates of the kinetic theory is the Boyle-Mariotte law that was evolved experimentally long before the kinetic theory of gases was elaborated. According to equations 1-15 and 1-16, it may be formulated as follows: *the product of the pressure and the volume of a certain mass of a gas is a constant value at a given temperature*, and, consequently, *when temperature is constant the volume of a given gas varies inversely as its pressure.*

Note that real gases do not conform exactly to the Boyle-Mariotte law.

The Gay-Lussac law. From equation 1-14 it follows that when p is constant

$$\frac{V}{T}=\frac{2}{3}\times\frac{Na}{p}=\text{const.} \tag{1-17}$$

This second result of the basic postulates of the kinetic theory constitutes Gay-Lussac's law which, like the Boyle-Mariotte law, was found experimentally. It may be formulated as follows: *when the pressure is constant the volume of a given mass of gas is directly proportional to its absolute temperature.*

For 1 kg of gas equation 1-17 may be written

$$\underline{\frac{v}{T}=\text{const}}$$

and, consequently, since $v = \frac{1}{\gamma}$

$$\boxed{\gamma T = \text{const}}, \tag{1-18}$$

i. e., the product of the specific weight of a given gas and its absolute temperature is a constant value for any given pressure.

Real gases do not conform exactly to this law, but show deviations from it.

Applying the Gay-Lussac law we may prove that absolute zero (0° K) is 273 divisions lower on the centigrade scale than the melting point of ice (0° C). Equation 1-17 may be expressed as follows:

$$\frac{V}{T} = \frac{V_0}{T_0} \text{ or } \frac{V}{V_0} = \frac{T}{T_0}$$

where T_0—0° C and V_0—the volume of the gas at that temperature. From the latter we get

$$\frac{V - V_0}{V_0} = \frac{T - T_0}{T_0}$$

and

$$\frac{V - V_0}{V_0 (T - T_0)} = \frac{1}{T_0}. \tag{1-19}$$

The left-hand part of the equation is nothing more than the difference in the volume of the gas when temperature is increased by one degree and its volume at 0° C; this is known as *the coefficient of expansion of gases at constant pressure.* Giving this coefficient the symbol α, we get

$$\alpha = \frac{1}{T_0} = \text{const}, \tag{1-20}$$

since the melting point of ice is constant and T_0 is, consequently, also constant. The truth of this has been established by numerous experiments which show that for the more perfect gases the coefficient of expansion is almost identical in all cases and is equal to the mean value of $\frac{1}{273}$. From equation 1-20 it follows that T_0 =273° K, the melting point of ice on the Kelvin scale, since zero on this scale is —273° C. *

* For gases that are almost ideal the coefficient of expansion is actually equal to $\frac{1}{273.16}$ and not $\frac{1}{273}$. It is, therefore, more accurate to take the values $T = 273.16$ and $T = 273.16 + t$. For the majority of calculations, however, $\alpha = \frac{1}{273}$ is sufficiently accurate.—*Ed.*

Avogadro's law. For gases with identical p, v and T, N is also the same, as follows from equation 1-14. This important theorem is formulated in Avogadro's law, which states that *equal volumes of different gases at the same pressure and temperature contain the same number of molecules*; in other words, the specific weight of gases, γ, at identical temperatures and pressures is directly proportional to their molecular weights μ, i. e.,

$$\frac{\mu}{\gamma} = \text{const},$$

and, since $\gamma = \frac{1}{v}$,

$$\mu v = \text{const}. \tag{1-21}$$

Equation 1-21 shows that when pressure and temperature are the same, the product μv is the same for all gases.

The quantity of gas by weight, μ (kg), where μ is its molecular weight, is called a *kilogram-molecule* or *mole*; the mole, therefore, will have a different value in kilograms for each different gas; a mole of oxygen weighs 32 kg and a mole of hydrogen 2.016 kg. Obviously the product μv is the volume of the mole (in cum) so that the equation 1-21 and Avogadro's law may be expressed in this way: *the volume of the mole is the same for all gases when temperature and pressure are the same.*

The specific weight of hydrogen, for example, is $\gamma = 0.09$ kcm at 0° C and 760 mm Hg; its molecular weight is, $\mu = 2.016$; therefore, for all gases under these conditions $\mu v = \frac{\mu}{\gamma} = \frac{2.016}{0.09} = 22.4$ cum (at 0° C and 760 mm Hg) (1-22)

and, given the same conditions,

$$\gamma = \frac{\mu}{22.4}. \tag{1-23}$$

This last-mentioned relation enables us to determine the specific weight of gases under *normal physical conditions* (0° C and 760 mm Hg, also known as standard temperature and pressure, abbreviated, STP) by their molecular weights and vice versa.

Real gases do not conform exactly to Avogadro's law.

1-5. The Equation of State for an Ideal Gas. For a mole of gas, equation 1-14 acquires the values

$$pV_\mu = \frac{2}{3} N_\mu a T, \tag{1-24}$$

where $V_\mu = \mu v$—the volume of the mole in cum;
N_μ — the number of molecules in a mole of gas;
a — the coefficient of proportionality, identical for all gases.

According to Avogadro's law, the volume of the mole V_μ is the same for all gases when p and T are the same; in this case, by equation 1-24, N_μ will also be identical for all gases, i. e., *the number of molecules in one mole is the same for all gases*, and it is, of course, the same at all pressures and temperatures. The number of molecules is known as *Avogadro's number*. Since the value of a is also the same for all gases, equation 1-24 may be written

$$pV_\mu = R_\mu T, \tag{1-25}$$

where

$$R_\mu = \frac{2}{3} N_\mu a = \text{const}, \tag{1-26}$$

which is known as *the universal gas constant*, the constant for one mole which is the same for all gases. Its magnitude may be determined by equation 1-25 if the volume of the mole, V_μ, is known for the given pressure and temperature. For example, according to equation 1-22, $V_\mu = 22.4$ cum when $p = 10{,}332$ ksm and $T = 273°$ K; equation 1-25, therefore, gives us

$$R_\mu = \frac{pV_\mu}{T} = \frac{10{,}332 \times 22.4}{273} = 848, \tag{1-27}$$

so that equation 1-25 becomes

$$pV_\mu = p\mu v = 848 \times T. \tag{1-28}$$

Equation 1-28 is for 1 mole, i. e., μ (kg) of gas; dividing by μ we get

$$pv = \frac{848}{\mu} T = RT \tag{1-29}$$

and the same equation applied to 1 kg of gas, where

$$R = \frac{848}{\mu} \tag{1-30}$$

is constant for 1 kg of the given gas, but has a different value for each different gas, depending on the molecular weight.

It follows from a comparison of equations 1-27 and 1-30 that

$$R_\mu = \mu R = 848. \tag{1-31}$$

Dividing equation 1-26 by N_μ, we get

$$k = \frac{R_\mu}{N_\mu} = \frac{2}{3}a = \text{const}, \tag{1-32}$$

where k is obviously nothing more than the gas constant for one molecule of gas; it is known as *Boltzmann's constant.*

Multiplying equation 1-29 by the real weight of the gas G (kg) we get (since $Gv=V$),

$$pV = GRT \tag{1-33}$$

which is the equation for G (kg) of gas.

Equations 1-28, 1-29 and 1-33 link together the basic values expressing the state of a gas—pressure, volume and temperature. Each of them is, therefore, *an equation of state, or a characteristic equation of an ideal gas.* They differ only in referring to different weights of gas. Equation 1-28 is the most general since it is applicable to one mole and is the same for all gases and gas mixtures. In many cases, the use of the mole and of equation 1-28 simplifies calculations, especially in cases of gas mixtures. The specific properties of a given ideal gas affect the calculation only when the specific volume is being determined by means of the relation $v=\frac{V_\mu}{\mu}$, since this includes the molecular weight of the given gas, μ.

Equations 1-29 and 1-33 differ for different gases because each gas has its own value for the constant R; this value can be determined either from equation 1-30 by the molecular weight of the gas μ, or from equation 1-29, if the specific volume of the gas v, or its specific weight γ, is known for definite pressures and temperatures. The value of the constant R can be obtained from equation 1-29; since $R=\frac{pv}{T}$ it will be measured in

$$\frac{\text{ksm} \times \text{cum-kg}}{\text{degrees}} = \text{kgm per kg} \times \text{deg.}$$

We do not cancel out the kg in this measurement, thereby indicating that R is the constant of 1 kg of gas; furthermore, it can be seen from this equation that the constant R is measured in units of work (kgm) which will be fully explained in paragraph 3-2.

It can be seen that the equation $pv=RT$ is a combination of Boyle-Mariotte's law and Gay-Lussac's law; actually when $T=\text{const}$, pv must also be constant (equation 1-16) and when $p=\text{const}$ $\frac{T}{v}=\gamma T=\text{const}$ (equation 1-18).

Since there are three variables in equation 1-29, p, v and T, it is obvious that only two of them can be independent; in other words, any pair of them, p and v, p and T or v and T may equally well determine the third and, consequently, the state of the gas.

When using equations of state it must be remembered that specific pressure p is measured in ksm.

Example 1-3. Air with a manometric pressure of 1 kscm expands to three times its volume, the temperature being constant. What is the absolute pressure at the end of the expansion if the height of the Hg barometer, reduced to 0° C, is 550 mm?

Absolute initial pressure

$$p_1=1+\frac{550}{735.6}=1.747 \text{ ata},$$

and according to Boyle-Mariotte's law

$$p_2=\frac{p_1}{3}=\frac{1.747}{3}=0.582 \text{ ata}.$$

Example 1-4. The gaseous products of combustion in the firebox of a steam boiler have a temperature of 1200° C at the beginning of the flue and 250° C at the end. By how many times has the volume been reduced during the cooling, assuming the same pressure at both ends of the flue?

By Gay-Lussac's law

$$\frac{v_1}{v_2}=\frac{T_1}{T_2}=\frac{273+1,200}{273+250}=\frac{1,473}{523}=2.82.$$

Example 1-5. Determine the volume of 1.4 kg of hydrogen ($R=420.6$) at a pressure of 2 ata and $t=25°$ C.

By equation 1-33

$$V=\frac{GRT}{p}=\frac{1.4\times420.6\times298}{20,000}=8.78 \text{ cum}.$$

Example 1-6. Determine the specific weight of nitrogen at 15° C and 1 ata and also its gas constant R, knowing that the molecular weight, μ, of nitrogen is 28.02.

By equation 1-30

$$R=\frac{848}{28.02}=30.26 \text{ kgm/kg}\times\text{deg},$$

and from equation 1-29

$$\gamma=\frac{1}{v}=\frac{p}{RT}=\frac{10,000}{30.26\times288}=1.148 \text{ kcm}.$$

We may also apply equation 1-28 and determine that

$$V_\mu=\frac{848T}{p}=\frac{848\times288}{10,000}=24.4 \text{ cum}.$$

And since

$$V_\mu=\mu v=\frac{\mu}{\gamma},$$

$$\gamma=\frac{\mu}{V_\mu}=\frac{28.02}{24.4}=1.148 \text{ kcm}.$$

Example 1-7. Determine the weight of oxygen (R=26.5) in a cylinder with a capacity of 100 litres at a temperature of 20° C; the pressure in the cylinder is 80 ata.

By equation 1-33

$$G=\frac{pV}{RT}=\frac{800,000\times0.1}{26.5\times293}=10.3 \text{ kg}.$$

Example 1-8. The specific weight of hydrogen at STP is 0.09 kcm; what would it be at 12 ata and 400° C?

Taking the characteristic equation 1-29 for both states of the gas, we divide the first equation by the second and get

$$\frac{p_1v_1}{p_2v_2}=\frac{T_1}{T_2} \text{ or } \frac{p_1}{p_2}\times\frac{\gamma_2}{\gamma_1}=\frac{T_1}{T_2},$$

whence

$$\gamma_2=\gamma_1\frac{p_2}{p_1}\times\frac{T_1}{T_2}=0.09\,\frac{120,000}{10,332}\times\frac{273}{673}=0.424 \text{ kcm}.$$

1-6. Gas Mixtures. Dalton's Law. If we are dealing with a mixture and not with a homogeneous gas, and 1 cum of the mixture contains n_1, n_2, etc., molecules of the different gases with masses of m_1, m_2, etc., the corresponding velocities being w_1, w_2, etc., and the temperature is uniform throughout the mass of the mixture, the kinetic energy of all the molecules (according to equation 1-13 will be the same); therefore,

$$m_1w_1^2=m_2w_2^2=\ldots=mw^2.$$

Thus, by equation 1-9, the pressure of the mixture will be

$$p=\frac{nmw^2}{3},$$

where n is the total number of molecules in the mixture;

$$n = n_1 + n_2 + \ldots$$

In view of this we may write

$$p = \frac{nmw^2}{3} = \frac{(n_1 + n_2 + \ldots)\, mw^2}{3} = \frac{n_1 m_1 w_1^2}{3} + \\ + \frac{n_2 m_2 w_2^2}{3} + \ldots = p_1 + p_2 + \ldots, \qquad (1\text{-}34)$$

where p_1, p_2, etc., are the pressures of the different gases on the walls of the vessel; these are known as *partial pressures.*

Equation 1-34 establishes *Dalton's* law which states *that when there is no chemical reaction the pressure of the gas mixture is equal to the sum of partial pressures of the different gases.*

The specific feature of gas mixtures, therefore, is that, in the absence of chemical reactions, each of the gases behaves, as though the other gases of the mixture did not exist, i. e., they expand to their full volume and exert the corresponding pressure on the walls of the vessel.

Real gases do not conform exactly to Dalton's law.

The composition of mixtures by weight and volume. In heat engineering homogeneous gases rarely occur; gas mixtures of various composition are most frequently met with, such, for example, as the products of fuel combustion or the fuel mixtures for gas engines. Gas mixtures conform fairly exactly to the equations of state:

$$pv = RT$$
$$pV = GRT$$
$$pV_\mu = 848T$$

but in order to apply the first two equations the gas constant R must be known; when the third equation is employed, in order to determine the specific volume $v = \frac{V_\mu}{\mu}$ we must know the *average* or *apparent molecular weight of the mixture*, μ, which is linked up with R by the relation $\mu R = 848$. Both μ and R naturally depend on the composition of the mixture, i. e., what gases are in the mixture and in what proportions.

The composition of a gas mixture is determined either by weight or by volume; in the first case the relative *weights*

of the components are used:

$$g_1 = \frac{G_1}{G}, \quad g_2 = \frac{G_2}{G}, \ldots, g_n = \frac{G_n}{G},$$

where $G_1, G_2, \ldots, G_n$ are the actual weights of the gases and G is the total weight of the mixture, so that

$$G = G_1 + G_2 + \ldots + G_n$$

and

$$g_1 + g_2 + \ldots + g_n = 1.$$

The determination of a mixture by volume requires some preliminary explanation. As we have said (Sec. 1-6), the specific feature of a gas mixture is that, in the absence of chemical reactions, each of the gases behaves as though the others did not exist in the mixture, i. e., each expands to its full volume and has its own equation of state from which we may compute the pressure according to the temperature and volume of the mixture.

This is known as the *partial pressure* of the components of the mixture; according to *Dalton's* law the total pressure of the mixture is the sum of the partial pressures.

The state of the component gases in the mixture is, therefore, characterised by the values,

$$\begin{array}{l} p_1, V, T; \\ p_2, V, T; \\ \ldots\ldots\ldots \\ p_n, V, T, \end{array}$$

where V and T are the volume and temperature of the mixture, and $p_1, p_2, \ldots, p_n$ are the partial pressures of the gases.

In order to compare quantities of the components of a mixture by their volumes, their volume V, which is relevant to the common temperature T, must be brought to a uniform pressure, the simplest being the pressure, p, of the mixture. The partial volumes of the mixture, $V_1, V_2, \ldots, V_n$, are obtained from Boyle-Mariotte's law from the relations:

$$\left.\begin{array}{l} pV_1 = p_1 V; \\ pV_2 = p_2 V; \\ \ldots\ldots\ldots \\ pV_n = p_n V. \end{array}\right\} \qquad (1\text{-}35)$$

The relations

$$r_1 = \frac{V_1}{V};\quad r_2 = \frac{V_2}{V},\ \ldots,\ r_n = \frac{V_n}{V}$$

are the *content of each of the component gases by volume* and determine the composition of the mixture.

By equation 1-35

$$V_1 = \frac{p_1}{p} V,\ V_2 = \frac{p_2}{p} V,\ \ldots,\ V_n = \frac{p_n}{p} V$$

and, applying Dalton's law

$$p_1 + p_2 + \ldots + p_n = p$$

so that

$$V_1 + V_2 + \ldots + V_n = \frac{p_1 + p_2 + \ldots + p_n}{p} V = V$$

and, consequently,

$$r_1 + r_2 + \ldots + r_n = 1.$$

There exists a simple relation between the quantities of the component gases measured by weight and by volume, connected by equations 1-21 and 1-30 for each gas separately

$$g_i = \frac{G_i}{G} = \frac{\gamma_i V_i}{\gamma V} = \frac{\mu_i}{\mu} r_i = \frac{R}{R_i} r_i \qquad (1\text{-}36)$$

(the specific weights γ and γ_i must be computed at the pressure, p, and temperature, T, of the mixture).

The gas constant and the apparent molecular weight of the mixture. From equation 1-36

$$r_i = g_i \frac{R_i}{R};$$

$$\sum r_i = \frac{\Sigma g_i R_i}{R} = 1,$$

whence

$$\underline{R = \sum g_i R_i = 848 \sum \frac{g_i}{\mu_i},} \qquad (1\text{-}37)$$

since

$$R_i = \frac{848}{\mu_i},$$

and, consequently, the apparent molecular weight of the mixture is

$$\mu = \frac{848}{R} = \frac{848}{\Sigma g_i R_i} = \frac{1}{\sum \frac{g_i}{\mu_i}}. \qquad (1\text{-}38)$$

Equations 1-37 and 1-38 serve to determine R and μ if the composition of the mixture is given by weight.

Again from equation 1-36

$$\sum g_i = \frac{\Sigma r_i \mu_i}{\mu} = 1,$$

whence

$$\mu = \sum r_i \mu_i = 848 \sum \frac{r_i}{R_i}, \qquad (1\text{-}39)$$

and, consequently,

$$R = \frac{848}{\mu} = \frac{848}{\Sigma r_i \mu_i} = \frac{1}{\sum \frac{r_i}{R_i}}. \qquad (1\text{-}40)$$

Equations 1-39 and 1-40 serve to determine μ and R if the composition of the mixture is given by volume.

Determination of partial pressures. Since, according to our determination of partial pressures and partial volumes

$$p_1 V = pV_1;\ p_2 V = pV_2;\ \ldots;\ p_n V = pV_n,$$

it follows that

$$\frac{p_1}{p} = \frac{V_1}{V} = r_1; \quad \frac{p_2}{p} = \frac{V_2}{V} = r_2; \ \ldots; \frac{p_n}{p} = \frac{V_n}{V} = r_n$$

and, consequently,

$$p_1 = r_1 p;\ p_2 = r_2 p;\ \ldots;\ p_n = r_n p. \qquad (1\text{-}41)$$

And since, by equation 1-36

$$r_i = g_i \frac{\mu}{\mu_i} = g_i \frac{R_i}{R}$$

then, simultaneously,

$$\left.\begin{aligned} p_1 &= g_1 \frac{\mu}{\mu_1} p = g_1 \frac{R_1}{R} p; \\ p_2 &= g_2 \frac{\mu}{\mu_2} p = g_2 \frac{R_2}{R} p; \\ &\ldots\ldots\ldots\ldots \\ p_n &= g_n \frac{\mu}{\mu_n} p = g_n \frac{R_n}{R} p. \end{aligned}\right\} \qquad (1\text{-}42)$$

Thus we see that the determination of partial pressures is very easy if the content by volume is given (equation 1-41); if the content by weight is given then the R or μ of the mixture must first be found (equation 1-42).

Example 1-9. The components of a generator gas are given by volume as

H_2	CO	CO_2	N_2
18%	24%	6%	52%.

Determine the weight of the components, the value of the partial pressures of each gas when the pressure of the mixture is 760 mm Hg, and the specific weight of the gas is taken at STP.

The molecular weights of the component gases are:

$$\mu_{H_2}=2.016;\quad \mu_{CO}=28;\quad \mu_{CO_2}=44;\quad \mu_{N_2}=28.02;$$

the apparent molecular weight of the generator gas, by equation 1-39 is,

$$\mu=\Sigma r_i\mu_i=0.18\times2.016+0.24\times28+0.06\times44+\\+0.52\times28.02=24.3,$$

and the specific weight at STP, by equation 1-23, is

$$\gamma=\frac{\mu}{22.4}=\frac{24.3}{22.4}=1.085 \text{ kcm}.$$

The weight of each component by equation 1-36 is

$$g_{H_2}=\frac{\mu_{H_2}}{\mu}r_{H_2}=\frac{2.016}{24.3}\times0.18=0.015;$$

$$g_{CO}=\frac{28}{24.3}\times0.24=0.276;$$

$$g_{CO_2}=\frac{44}{24.3}\times0.06=0.109;$$

$$g_{N_2}=\frac{28.02}{24.3}\times0.52=0.6;$$

so that the composition by weight is

H_2	CO	CO_2	N_2
1.5%	27.6%	10.9%	60%.

The partial pressures by equation 1-41 are

$$p_{H_2}=r_{H_2}p=0.18\times760=136.8 \text{ mm Hg};$$
$$p_{CO}=r_{CO}p=0.24\times760=182.4 \text{ mm Hg};$$
$$p_{CO_2}=r_{CO_2}p=0.06\times760=45.6 \text{ mm Hg};$$
$$p_{N_2}=r_{N_2}p=0.52\times760=395.2 \text{ mm Hg}.$$

Example 1-10. Determine the gas constant, specific weight at STP, and the composition by volume of a mixture consisting of 95% air and 5% fire damp (gas constant, $R_f=73.5$).

The gas constant of dry air, R_a, is 29.27; therefore, applying equation 1-37, we get

$$R=\Sigma g_i R_i=0.95\times 29.27+0.05\times 73.5=31.47$$

and the apparent molecular weight by equation 1-38 is

$$\mu=\frac{848}{R}=\frac{848}{31.47}=26.9.$$

By equation 1-23, the specific weight at STP is

$$\gamma=\frac{\mu}{22.4}=\frac{26.9}{22.4}=1.2 \text{ kcm}.$$

By equation 1-36, the content by volume is

$$r_a=g_a\frac{R_a}{R}=0.95\times\frac{29.27}{31.47}=0.885;$$

$$r_f=g_f\frac{R_f}{R}=0.05\times\frac{73.5}{31.47}=0.115,$$

i. e., air constitutes 88.5% of the volume and fire damp 11.5% of the volume.

Example 1-11. Determine the gas constant of a fuel mixture consisting of 1.3 cum of air and 1 cum of gas, if the latter has a specific weight of 1.2 kcm at STP.

The quantities of air and gas by volume are

$$r_a=\frac{1.3}{2.3}=0.565 \text{ and } r_g=\frac{1}{2.3}=0.435.$$

Applying equation 1-23, the molecular weight of the gas is

$$\mu_g=22.4\times 1.2=26.9$$

and the molecular weight of the air (as per table) $\mu_a=29$. Therefore, applying equation (1-40) we get

$$R=\frac{848}{\Sigma r_i\mu_i}=\frac{848}{0.565\times 29+0.435\times 26.9}=30.2.$$

1-7. Real Gases. Their Deviations from the Ideal Gas Equations. The characteristic equation $pv=RT$ which we obtained by applying the postulates of the kinetic theory of gases is, strictly speaking, true for ideal gases only, that is for gases in which there is no molecular attraction and the volume occupied by the molecules is infinitely small as compared with the total volume occupied by the gas. Such gases do not exist in nature; it is therefore obvious that all real

gases deviate to some extent from the equation $pv=RT$, that is, from the Boyle-Mariotte and Gay-Lussac laws of which it is a combination.

We know from physics that all real gases, when cooled below *the critical temperature* (t_{cr}), established by Mendeleyev, and simultaneously compressed, change into fluids; to put it another way, all gases are the superheated vapours of certain fluids. Molecular attraction is considerable in all fluids so that the closer a gas is to transition into a fluid state the greater its deviation from the properties of an ideal gas; the farther it is from the fluid state, the closer its approximation to a real gas. The very fact that Boyle-Mariotte's law and Gay-Lussac's law were established by pure experiment shows that in many cases real gases are close to the ideal state. All biatomic gases—hydrogen, nitrogen, oxygen, air, carbon monoxide (CO)—belong to this category; in their practical use in heat engineering they are usually far removed from the fluid state because their critical temperatures are much lower than 0° C.

Gas	H_2	N_2	CO	Air	O_2
t_{cr}	−242°	−147.1°	−141°	−140.6°	−118.8° C

In general, the deviation of real gases from the ideal state increases as temperature decreases and pressure increases.

Van der Waals equation. Deviations of real gases from the ideal state $pv=RT$ may be calculated with sufficient accuracy by applying the following equation:

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT, \qquad (1\text{-}43)$$

where a and b are constants for the given gas.

Comparing equation 1-43 with the equation of the ideal state $pv=RT$, we see that two new corrections are made to the ideal state: $(+a)$ for pressure, and $(-b)$ for volume.

We may transpose equation 1-43 as

$$p=\frac{RT}{v-b}-\frac{a}{v^2} \qquad (1\text{-}44)$$

and explain it as follows from the point of view of the kinetic theory. For an ideal case, i. e., one in which the volume of the molecules and their mutual attraction is ignored, $p=\frac{RT}{v}$. The finite volume of the molecules of a real gas, by

reducing the free space in which the molecules move, increases the number of impacts on the walls of the vessel and, consequently, the pressure p, which is equivalent to gas being reduced by some value b, i. e., by the relation $\frac{v}{v-b}$, as shown by the first member of the right-hand part of equation 1-44. The presence of molecular attraction, creating an internal gas pressure, p_i, reduces the pressure, p, on the walls, because each molecule, influenced by the attraction of its neighbours, approaches the walls of the vessel at a reduced velocity. This reduction in the pressure on the walls is equal to the internal pressure p_i which has a direction towards the centre, away from the walls, and is directly proportional to the number of molecules colliding with each square metre of the walls and the number of molecules attracting them away from the walls, i. e., the square of the number of molecules per sq m, which, in turn, is directly proportional to the specific weight γ, and, therefore, inversely proportional to the specific volume v. The internal pressure p_i must, therefore, be inversely proportional to v^2, i. e., $p_i=\frac{a}{v^2}$, where a is a constant depending on the nature of the gas. The pressure p of the gas on the walls is reduced by the value of p_i, as shown in equation 1-44.

As we have said, the Van der Waals equation reflects the properties of real gases with sufficient accuracy; in a number of cases, however, it deviates noticeably from results obtained experimentally. A number of attempts have been made to produce a more exact equation, all of which necessarily make it more complicated.

A much more precise result may be obtained by applying the equation for real gases elaborated by Professors Vukalovich and Novikov (1939); in addition to molecular attraction and the influence of the volume of the molecules, this equation also includes the phenomenon of molecular association which consists in individual molecules uniting to form double and triple molecules; the gas, therefore, is not homogeneous but is a mixture of gases consisting of individual, double and triple molecules. This equation is an improved Van der Waals equation and is more accurate in depicting the state of real gases.

In our further investigations of the thermodynamic properties of gases we shall apply the equation $pv=RT$ which has the advantage of simplicity and, as we have already said,

the majority of real gases as used in engineering may quite well be described by the equation for ideal gases. We must further point out that $pv = RT$ reflects a *state of equilibrium* when the pressure, temperature and specific volume (or specific weight) are the same at any moment throughout the entire mass of the gas; this state is called equilibrium because the body can only be brought out of this state by outside influences.

Chapter Two

THE FIRST LAW OF THERMODYNAMICS

2-1. The Equivalence of Heat and Work. At the very dawn of history man learned by experience that mechanical energy or work will produce heat, and made use of this experience when rubbing together two pieces of dry wood or striking a flint to obtain fire. Practical proof of the possibility of converting heat into work was given by the first steam engines set in motion by the heat produced in boiler fire-boxes by the combustion of fuel.

Heat, like every other form of energy, is quantitatively measurable; the technical unit is the *Calorie*, the amount of heat needed to raise the temperature of 1 kg of water by 1° C. Since this amount varies together with the temperature, even if only insignificantly, the Soviet Standard (OCT 6259) defines the Calorie as the amount of heat required to raise the temperature of 1 kg of water from 19.5° to 20.5° C (known as the 20° Calorie). This definition is practically the mean between temperatures from 0 to 100° C, i. e., one hundredth of the amount of heat needed to raise the temperature of 1 kg of water from 0 to 100° C. This technical Calorie is also known as *the great calorie* or *kilogram-calorie* (Cal, spelt with a capital C—is the abbreviation we shall use) to distinguish it from the *gram-calorie* (cal) used in physics and amounting to 0.001 of a technical Calorie.

The technical unit of work is the *kilogram-metre* (kgm).

According to the law of the conservation of energy, discovered by Lomonosov, *heat and work are the equivalents of each other* and may be converted one into the other, following the law of proportionality:

$$\boxed{Q = AL} \qquad (2\text{-}1)$$

where Q—the amount of heat in Cal that is converted into work;

L—the work in kgm obtained from Q;

A—a constant multiplier, the coefficient of proportionality.

We see from this that there is a definite relation between the units of heat and work so that it is quite in order to measure heat in kgm and work in Cal.

The equivalence of heat and mechanical energy (work) led to the formulation of the general law of the conservation of energy which states that energy can be neither created nor destroyed but only converted from one form into another and that the amount of energy in one form that "disappears" during the conversion is replaced by an equal amount of the new form. The equivalence of heat and work is obviously a particular case of the general law and is not connected with any specific concepts of the nature of heat energy and the structure of matter. From the point of view of the kinetic theory of heat and matter the equivalence of heat and work is a foregone conclusion since that theory states that the heat of a material body is nothing but the mechanical energy of the movements of its minutest particles, the molecules and atoms.

The constant multiplier of equality 2-1,

$$A = \frac{Q}{L},$$

determines the number of Cal that are the equivalent of 1 kgm and is therefore known as *the heat equivalent of work*. Its magnitude was determined experimentally; the first accurate measurements were made in the forties of the last century and produced a mean figure of $A = \frac{1}{424}$ Cal/kgm, which was considered accurate up to the end of the century. Today the figure obtained as the result of later investigations is taken as

$$\boxed{A = \frac{1}{427}\ \text{Cal/kgm}}. \qquad (2\text{-}2)$$

The inverse magnitude of the heat equivalent

$$\frac{1}{A} = \frac{L}{Q} = 427\ \text{kgm/Cal},$$

determines the number of kgm that are the equivalent of 1 Cal, and is called *the mechanical equivalent of heat.* Both the heat and mechanical equivalents, therefore, are multipliers to be used in converting kgm into Cal and vice versa.

The principle of the equivalence of heat and work may be given the following detailed formulation: *in the conversion of heat into work every kgm of work provides 1/427 Cal of heat and, consequently, every "vanishing" Cal provides 427 kgm of work.* The simplest expression of this relation is

$$1 \text{ Cal} = 427 \text{ kgm},$$

from which we see that the great calorie is a much bigger unit of energy than the kilogram-metre.

In general the kilogram-metre is too small a unit for industrial use and in power engineering the *horse-power hour* is used. Horse power (hp) is the industrial unit of power, the work done in one second, i. e.,

$$1 \text{ hp} = 75 \text{ kgm/sec}$$

from which we get

$$1 \text{ hp-hr} = 75 \times 60 \times 60 = 270{,}000 \text{ kgm},$$

which in heat units is

$$1 \text{ hp-hr} = \frac{270{,}000}{427} = 632 \text{ Cal}.$$

The industrial unit of electrical energy is the *kilowatt-hour* (kwh), the work of one kilowatt for one hour. The kilowatt (kw) is the industrial unit of electric power, and,

$$1 \text{ kw} = 102 \text{ gm/sec} = 1.36 \text{ hp},$$

therefore,

$$1 \text{ kwh} = 102 \times 60 \times 60 = 367{,}200 \text{ kgm} = 1.36 \text{ hp-hr}$$

which, expressed in heat units is

$$1 \text{ kwh} = \frac{367{,}200}{427} = \underline{860 \text{ Cal}.}$$

In connection with this the London International conference on steam tables, held in 1929, defined the Calorie as the amount of heat equivalent to $\frac{1}{860}$ kwh (*"the international great calorie"*). This definition is superior to those given earlier since it excludes the dependence of the Calorie on

temperature, latitude and height above sea-level, insofar as gravitational acceleration and, therefore, the mass of 1 kg water depends on those factors. The kilowatthour is a unit that is definite, is measurable with great precision and is universally accepted, not only in Europe, but in Britain and the U.S.A. as well; the international Calorie, therefore, deserves universal recognition and application.

Example 2-1. When a steam engine was being tested it was found that each kg of the exhaust steam contained 70 Cal less heat than that supplied to the engine and that the engine generated 150 hp, consuming 1,400 kg of steam per hour. Assuming that the "vanishing" 70 Cal per kg of steam were all converted into work, determine the magnitude of the mechanical equivalent of heat on the basis of this test.

The full amount of heat converted into work in one hour:

$$Q = 70 \times 1{,}400 = 98{,}000 \text{ Cal},$$

and the work of the engine in the same time (1 hp = 75 kgm/sec).

$$L = 75 \times 150 \times 60 \times 60 = 40{,}500{,}000 \text{ kgm};$$

therefore, by equation 2-1

$$\frac{1}{A} = \frac{L}{Q} = \frac{40{,}500{,}000}{98{,}000} = 413 \text{ kgm/Cal}.$$

The figure obtained is naturally less than the true figure (427 kgm/Cal) because less than 70 Cal per kg of steam were used for the work on account of losses by radiation, etc.

Example 2-2. 1 kg of good coal produces 7,800 Cal of heat when fully consumed. How far would a train go on 1,000 kg of coal if 10 % of the heat generated by the coal in the locomotive fire-box is converted into work, the resistance of the train to movement is 5 kg per ton weight of the train and the train weighs 2,000 tons?

The amount of heat converted into work by the combustion of 1,000 kg of coal

$$Q = 0.1 \times 7{,}800 \times 1{,}000 = 780{,}000 \text{ Cal}.$$

The work equivalent of this heat (equation 2-1) is

$$L = \frac{Q}{A} = 427 \times 780{,}000 = 333{,}000{,}000 \text{ kgm}.$$

The resistance of the train to movement, or the tractional power of the locomotive

$$P = 5 \times 2{,}000 = 10{,}000 \text{ kg};$$

therefore, the distance run

$$a = \frac{L}{P} = \frac{333{,}000{,}000}{10{,}000} = 33{,}300 \text{ m} = 33.3 \text{ km}.$$

Example 2-3. The boiler house of a power station consumes 20 tons of coal in six hours, the combustion of each kg of coal giving 7,000 Cal

of heat. Determine the electric power generated by the station if 20% of the heat obtained from the coal is converted into electric energy.

The amount of heat converted into electric energy in six hours work.

$$Q = 0.2 \times 7{,}000 \times 20 \times 1{,}000 = 28{,}000{,}000 \text{ Cal}$$

and the equivalent amount of electric energy or work, since 1 kwh = 860 Cal, would be

$$L = \frac{Q}{860} = \frac{28{,}000{,}000}{860} = 32{,}560 \text{ kwh},$$

therefore the average electric energy generated by the station

$$N_e = \frac{32{,}560}{6} = 5{,}420 \text{ kw}.$$

2-2. The First Law of Thermodynamics. If a body with a weight G (kg), a volume V, temperature t, and having a certain external pressure bearing on its surface, has an infinitely small quantity of heat dQ, imparted to it externally, in the general case the temperature of the body is raised by dt and the body expands, increasing its volume by dV.

An increase in temperature means an increase in the kinetic energy of the molecular and intramolecular motion of the particles of the body, which is the modern conception of heat energy—i. e., an increase in the velocity of the particles. In other words, there is an increase in the *internal kinetic energy of the body* which we perceive as an increase in temperature; we shall express this in units of work (kgm), using the symbol dK.

The increased volume of the body is due to the increased distance between the molecules and since, in the general case, there is mutual attraction between the molecules, the increase in the distance between them involves a certain amount of *internal work, the work of dispersion*, which goes to increase the potential energy of the particles of the body, i. e., *increases the internal potential energy of the body* which we shall express in units of work, using the symbol dP.

In some cases the increased distance between the molecules leads to a change in the structure of the body, converting it from a solid into a fluid (*melting*) or from a fluid into a vapour (*vaporising*).

The increased volume of the body, furthermore, involves more work in overcoming the external pressure—i. e., *external work* which we shall express by the symbol dL'.

Assuming that no other changes take place in the body (chemical or electrical, for instance), by the law of the conservation of energy and the principle of the equivalence of heat and work, we get the heat balance equation which uses the above-mentioned symbols:

$$dQ = A\,(dK + dP + dL') = A\,(dK + dP) + AdL'.$$

The first member of the right-hand part is obviously the sum of the increase in the internal kinetic and potential energy of the body, or, more briefly, the increase in the *internal (heat) energy of the body in heat* units; introducing the relation

$$A\,(dK + dP) = dU$$

we get

$$\boxed{dQ = dU + AdL'.} \qquad (2\text{-}3)$$

Equation 2-3 establishes what is known as the *first law of thermodynamics* which states for the general case, the above postulates considered, that *the heat dQ, imparted to a body, is expended in two directions: part of it is used to increase the internal energy of the body dU, and the remainder, AdL', on its equivalent is external work, dL'*. In deducing equation 2-3 we ignored the possible chemical and electrical changes that may occur when heat is imparted to a body and also changes in the external kinetic energy of the body, that is, the energy of its visible movement, with the result that we produced a very simple formula that is convenient for research work since it expresses the basic relations involved in the conversion of heat into work. This equation is basic in thermodynamics and in future we shall constantly be applying it.

Each of the three members of this equation can be positive or negative, depending on circumstances, and in some cases they may equal zero; if heat is imparted to the body then $dQ>0$, if it is taken from the body then $dQ<0$; if the internal energy of the body increases, $dU>0$, if it decreases, $dU<0$; if the body expands and as a result does the work of overcoming the external pressure, $dL'>0$; in the case of compression, when external work is obviously expended, $dL'<0$.

If $dQ=0$, that is, if no heat is imparted to or taken from the body, in other words, if there is no exchange of heat between

the working body and the surrounding medium or other bodies, then, by equation 2-3

$$AdL' = -dU,$$

i. e., a special case in which work may possibly be effected exclusively by a reduction of the internal energy of the body. The change in the state of a body, or the *process*, which takes place without heat exchange ($dQ=0$) is known as the *adiabatic process* and plays an important role in thermodynamics both in theory and practice. In cases of adiabatic compression the whole of the external work expended on it ($dL'<0$) goes to increase the internal energy of the body.

If $dL'=0$ the volume of the body obviously does not change, i. e., $V=\text{const}$; such a process is *isochoric* and equation 2-3 takes on the form

$$dQ = dU,$$

i. e., the heat imparted to the body is used entirely in increasing the internal energy.

If, finally, $dU=0$, i. e., the internal energy of the body does not change, ($U=\text{const}$), then

$$dQ = AdL',$$

i. e., the heat imparted to the body is transformed entirely into external work; this process is called *isodynamic.*

In the general case there is no equivalence between the heat dQ imparted to the body and the work dL' performed by it because it is not the amount of heat dQ that is converted into work, but an amount equivalent to the work

$$AdL' = dQ - dU;$$

$AdL'<dQ$ when $dU>0$, that is, if the internal energy of the body increases; $AdL'>dQ$ when $dU<0$, that is, if the internal energy of the body diminishes; in this latter case external work is obtained both from the imparted heat dQ and from the reduction in the internal energy of the body.

The first law of thermodynamics, therefore, is simply the law of the conservation of energy applied to thermodynamic processes.

For a body of 1 kg we shall express equation 2-3 as

$$\boxed{dq = du + Adl'} \qquad (2\text{-}4)$$

where

$$dq = \frac{dQ}{G}; \quad du = \frac{dU}{G}; \quad dl' = \frac{dL'}{G}.$$

2-3. The Internal Energy of a Body. As we have said, by the internal energy of a body we understand the sum of the kinetic and potential energies of the minute particles of the body (atoms and molecules) that are due: first to the velocity and mass of the particles, secondly to their disposition in respect of each other and to the forces of attraction. Therefore every body in a given state possesses a certain internal energy determined by that state. In other words the internal energy u is a function of the state of the body, or, more precisely, a magnitude describing that state (in the general case p, v, t), so that du is the full differential of this function. Thus, when the body is converted from state 1, described by the magnitudes p_1, v_1, t_1 to state 2, described by the magnitudes p_2, v_2, t_2, we obtain the changes in the internal energy of a body of 1 kg as

$$\int_1^2 du = u_2 - u_1,$$

where u_1 is the internal energy per kg of the body in its initial state and u_2 in its final state, i. e., the *change in the internal energy of the body is fully determined by the initial and final states of the body and is not dependent on the intermediate states* or, consequently, on the conditions under which the body changes from one state to the other or, technically speaking, *on the nature of the process.*

Since any body with a weight G possesses a certain internal energy $U = Gu$, the internal energy of 1 kg of the body u is characteristic of the state of the body in the same way as p, v, t; like them it may serve to determine its state. We know from equation 2-4 that we measure the internal energy in heat units (Cal); some scientists measure it in units of work (kgm) so that their equation 2-4 will be

$$dq = A\,(du + dl'),$$

and although at first glance the difference between the two cases is very great it is actually insignificant since heat and work are equivalent and either of them can be measured in Calories or in kilogram-metres. The most widespread method, however, is the measurement in Calories.

In some cases the equation is further simplified (proceeding from the same consideration) to:

$$dq = du + dl'$$

which ignores the heat equivalent $Au\ dl'$, and which we do not consider a fortunate simplification.

2-4. The Work of Expansion. Let us suppose that a homogeneous body with the weight G and volume V (Fig. 2-1) under an equally distributed external pressure, p, that is balanced by the resilience of the body (i. e., the external pressure is equal to the pressure of the body on the surrounding medium) has imparted to it an infinitely small amount of heat dQ which causes the volume to increase to $V+dV$ (the broken line). In its initial state a pressure $p\ df$ is exerted on the element of its area df, perpendicular to the surface both inwards and outwards. As the body expands to dV the surface is shifted perpendicularly to ds and the pressure on the body $p\ df$, which, in the course of the infinitely small shift may be regarded as constant, performs the *work* $p\ df\ ds$. The elementary work of the whole body—*the work of expansion*—is

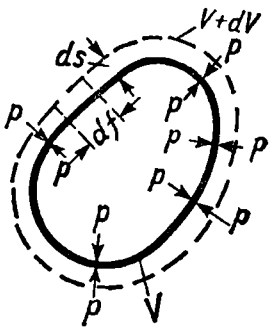


Fig. 2-1

$$dL = \int p\ df\ ds = p \int df\ ds,$$

but $\int df\ ds$ is obviously merely the increase in the volume of the body dV; therefore

$$\boxed{dL = p\ dV.} \qquad (2\text{-}5)$$

In the case under examination the expansion dL is simultaneously the *external work* dL' since the pressure of the body p is the same as the external pressure. In general, however, the external work does not always equal the work of expansion. Equation 2-5, where p is the specific pressure of the body, always gives us the elementary work of expansion but gives us the elementary external work only in cases of equilibrium.

Equation 2-5 for the elementary work of expansion was obtained by assuming the expansion of the body in all directions, but it is true for all cases of changes in volume, in

particular for expansion in one direction. We can demonstrate this by the simple practical example of a piston in a cylinder. The movable piston K is a tight fit in the metal cylinder C with a cover D (Fig. 2-2); the left-hand part of the cylinder contains any gas (or vapour) at specific pressure p. If the cylinder walls and the cover are nonresilient an infinitely small expansion of the gas to dV will cause an infinitely small shift of the piston to the right, ds, to the position of the dotted line; $dV=F\,ds$, where F is the area of the piston, or the cross section of the cylinder, which is the same thing. In this case, therefore, the work is in the form of the entire pressure of the gas exerted on the piston $P=pF$, and according to the laws of mechanics is

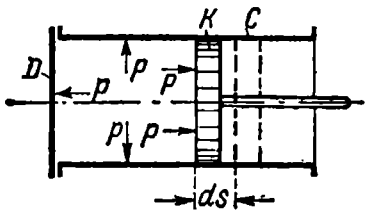


Fig. 2-2

$$dL = P\,ds = pF\,ds = p\,dV.$$

As we see, the work of the body is indissolubly bound up with changes in volume and is determined by that volume and the specific pressure when V is constant, i. e., when $dV=0$ and $dL=0$. Moreover, since the absolute pressure p is always a positive magnitude, dL and dV have the same signs: if $dV>0$ then $dL>0$ also, i. e., during expansion the work of the body is positive or "the body is performing work"; if $dV<0$ then $dL<0$ also, i. e., in cases of compression the work of the body is negative—work is performed on the body, work from outside is expended to cause the compression.

For 1 kg of the body, equation 2-5 is expressed as

$$dl = p\,dv. \qquad (2\text{-}6)$$

The work of 1 kg of the body, when there is a finite change in the volume from v_1 to v_2, can be computed by integrating equation 2-6 between these limits

$$l = \int_{v_1}^{v_2} p\,dv.$$

With regard to this last expression, it must be mentioned that in the general case, since the specific pressure p is a variable, the integration, and consequently the computation of the work, is only possible when the functional depend-

ence existing between the two variables p and v is given, in other words, when it is known how the pressure changes with the volume. If this functional dependence is given, e. g., $p=\varphi(v)$, then the calculation of the work

$$l=\int_{v_1}^{v_2} p\,dv=\int_{v_1}^{v_2}\varphi(v)\,dv$$

is reduced to finding a definite integral of the function $\varphi(v)$ for dv within the limits of the variable v from v_1 to v_2—a problem that is definite and permits of only one solution.

If the functional dependence of p on v is given for the time of the process then it can be found graphically, as we know from analytical geometry, by a right-angled coordinate system with two axes; we mark off the different values of the specific volume v within the limits v_1—v_2 on the axis of the abscissa and the corresponding values of p, found by applying the equation $p=\varphi(v)$ on the axis of the ordinate and we get a number of points that in the general case make the curve ab (Fig. 2-3) showing that p is a function of v; this is usually

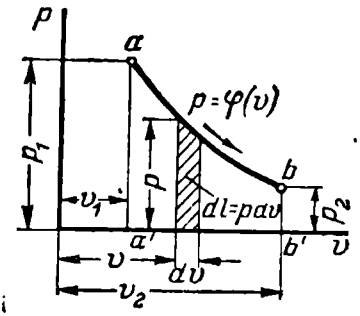


Fig. 2-3

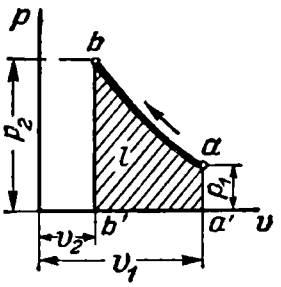


Fig. 2-4

called *the pressure curve*, and the diagram is known as the pressure-volume or pv diagram. Each point on the curve gives the momentary values of the specific pressure p and the specific volume v and the curve as a whole shows the changes of pressure depending on volume for the time of the process; the curve ab, therefore, is the graphic depiction of a definite change in the state of a body in the system pv—in short, it is the *curve of the process*.

For an infinitely small dv the area of the vertical shaded strip represents $p\,dv = dl$; therefore the work of the process ab

$$l = \int_{v_1}^{v_2} p\,dv$$

is depicted, on a scale determined by the scales of the coordinates, as area $abb'a'$ bounded by the curve of the process, the axis of the abscissa and the end ordinates, in brief, by the area below the pressure curve. In Fig. 2-3 the point a is the beginning of the process (p_1, v_1) and point b the end (p_2, v_2) and the arrow on the curve shows the direction of the process; we see that this is a process of expansion ($v_2 > v_1$) so that the work l is positive. In the case represented by Fig. 2-4 we have a process of compression ($v_2 < v_1$) so that work l will be negative.

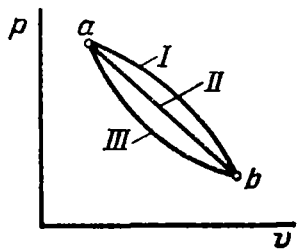


Fig. 2-5

Thus, from the graph of a process in the pv system we obtain a clear conception of how the pressure p and the volume v change, we know whether the body expands or contracts, and can determine the work l as the area below the curve of the process; for this reason the graph of a process in the pv system is often called the *working diagram*.

Under the conditions given in Fig. 2-1, where the pressure of the body and the external pressure are equal, $dl = dl'$, and equation 2-4 for 1 kg of the body may be expressed as

$$dq = du + A\,dl,$$

and for any finite change in the state of a body it is expressed as

$$\boxed{q = u_2 - u_1 + Al.} \qquad (2\text{-}7)$$

A change in the internal energy as a function of the state of the body is determined by the difference $(u_2 - u_1)$ between its value at the end and beginning of the process, irrespective of the character of the process. The value of the work l is not determined by the initial and final state of the body, but depends on the nature of the process, as can be seen clearly from the working diagram (Fig. 2-5). To use this diagram to determine the work, the points a and b are clearly insuffi-

cient, since they give only the coordinates of the pressure p and the volume v at the beginning and end of the process; it is necessary to have the whole curve of the process ab; the different pressure curves, *I*, *II*, *III*, with common points a and b, correspond to different areas of work. Work, therefore, *is not a function of the state of the body* but a function of the process. Since the work l is not a function of the state of the body, *dl is not a full differential* like du; for a finite process, therefore, we have l and not (l_2-l_1) which would be meaningless.

Since the value of the work l depends on the nature of the process, *the quantity of heat q that is imparted to the body*, as the algebraic sum of the changes in the internal energy and the work, must also *depend on the nature of the process*, i. e., not only on the initial and final state of the body but also on the conditions of the transition of the body *from one state to the other*. In other words, the heat q, like the work l, is not a function of the state of the body but a function of the process, and dq is *not a full differential*; for a finite process, therefore, we have q and not (q_2-q_1) which would be meaningless. Generally speaking, it should be said that as dq and dl are not full differentials some other symbols might be used, e. g., δq and δl; the above explanation, however, makes this unnecessary.

The change in internal energy (u_b-u_a) is identical for all three processes (Fig. 2-5); as far as the work is concerned, it is obvious that $l_{\mathrm{I}}>l_{\mathrm{II}}>l_{\mathrm{III}}$ so that $q_{\mathrm{I}}>q_{\mathrm{II}}>q_{\mathrm{III}}$.

Since the heat is converted into work as a result of the expansion of the body, it will be understood that in practice the most suitable body is one that permits of a considerable increase in its volume. This property is possessed by gases and the vapours of various fluids; the fluids themselves and solid bodies undergo an insignificant change in volume. The working body used in heat engines consists of gases, i. e., the gaseous products of the combustion of some fuel (internal combustion engines), steam (water vapour) and sometimes mercury vapour (steam engines and turbines).

2-5. Reversible and Irreversible Processes. The gas equation of state for ideal gases, $pv=RT$, connects the three main values—specific pressure, specific volume and temperature—that show the state of a gas assumed to be homogeneous, i. e., when it is assumed that these three values, that in the gener-

al case vary with time, are identical at any given moment in all parts of the gas. A gas that answers these requirements is said to be in a *state of equilibrium*, a state that cannot change without outside interference; if the pressure and temperature differ in different parts of the body and the body is left undisturbed, i. e., isolated from all external influences, both the temperature and the pressure will equalise after a certain time has elapsed. Uniform pressure is the condition for *mechanical equilibrium* and uniform temperature for *thermal equilibrium*; the equation of equilibrium, therefore, is true for a gas when both these conditions are fulfilled.

Equilibrium in a gas not contained in a rigid vessel with heat insulation is obviously only possible when the pressures and temperatures inside and outside the gas are the same; a reduction in the external pressure causes the expansion of the gas to the point when the pressures are again equal and the gas once more attains its state of equilibrium after passing through a series of stages where it is out of equilibrium; some time is required for this because pressure changes at the surface of a gas are only gradually transmitted through the entire mass at a certain finite velocity.

Similarly a rise in the temperature of the surrounding medium will bring about a rise in the temperature of the gas which will be gradually transmitted from the periphery inwards, but some time will elapse before the gas is equalised with the surrounding medium and is again in a state of equilibrium. From this it follows that the transition from one state of equilibrium to another is only possible when the first state has been disturbed externally; during the transition the gas passes through a number of states in which equilibrium is not maintained.

Insofar as the gas equation of state is true only of gases in a state of equilibrium, by applying it to a process we are establishing the fact that the latter consists of an unbroken series of states of equilibrium. The contradiction disappears if we assume that a change in the pressure and temperature of the surrounding medium and, consequently, of the gas, takes place at an infinitely slow rate, so that at every moment the differences in the pressures and temperatures of the gas and the surrounding medium, to say nothing of their differences inside the gas mass, are infinitely small; assuming this condition, it may be said that the process is one of an unbroken series of states of equilibrium and that we may

apply the equation of equilibrium to it throughout its course. A graph in which the coordinates *pv* are points showing the state of the gas will produce a continuous curve for the process, similar to that in the previous paragraph, only when there is mechanical and thermal equilibrium, when the pressure and temperature, and consequently the specific volume, are the same throughout the entire mass of the gas. It follows, therefore, that only balanced processes can be depicted graphically with precision; when a graph is used to depict processes out of equilibrium they must necessarily be conventional approximations.

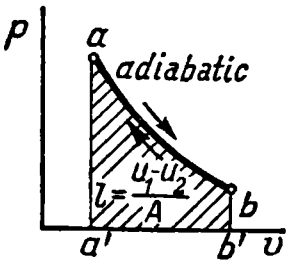


Fig. 2-6

Mechanical and thermal equilibrium are essential for a process *to be reversible*, i. e., for it to proceed in opposite directions, with both the working body and the surrounding medium that takes part in the process going through the same series of states in both directions but in the reverse sequence. In this case, if we have, for instance, a reversible process of the adiabatic (without the transfer of heat from the surrounding medium) expansion of a gas *ab* (Fig. 2-6), the ordinates of the curve *ab* give not only the value of gas pressure but also that of the external pressure. If the external pressure is raised when the gas reaches the state indicated by point *b*, the gas will go through the reverse process *ba* and by adiabatic compression will return to its initial state at point *a*; the work *l*, expended externally on compressing the gas, will be equal to the work previously expended on expansion. The result of these reversible converse and reverse processes is that the gas and the surrounding medium do not undergo any changes in returning to their initial state.

When mechanical and thermal equilibrium are absent the process is *not reversible*, i. e., either it is, in general, not feasible in the reverse direction, or the reverse process takes place with different parameters; in any case, neither the gas nor the surrounding medium is returned to its initial state by the reverse process.

When there is a noticeable difference between the pressure of the gas and that of the surrounding medium, the gas expands or contracts rapidly and this gives rise to vortical movements that take a certain time to reach a state of repose,

their energy being transformed into heat energy which is absorbed by the gas together with the externally applied heat. The fact that this process is irreversible is clearly demonstrated by the following example. Let there be two vessels of equal capacity V connected by a pipe with a cock (Fig. 2-7); the left-hand vessel contains gas at pressure p_1 and temperature t_1, and the right-hand vessel has been fully exhausted so that the pressure is equal to zero. When the cock is opened the gas expands rapidly and flows from the left-hand to the right-hand vessel at high velocity until there is equal pressure in both vessels The strong vortices set up in the gas during the transfer subside in time and the gas in the two vessels attains a new state of equilibrium.

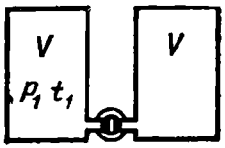


Fig. 2-7

It is obvious that this process is not reversible in practice since the return of the gas from the final to the initial state would involve its return from the right-hand to the left-hand vessel which is impossible without the expenditure of external work on its compression, whereas in the original process no external work was expended.

As we see the given process is irreversible on account of the need to expend external work on its return; when the gas expanded to double its original volume no external work was expended.

Unless there is thermal equilibrium a process is also irreversible. If, during the original process, the body transfers heat to the surrounding medium whose temperature is noticeably lower than that of the body, the reverse process, i. e., the imparting of heat from outside, would only be possible if the temperature of the surrounding medium were raised to at least the temperature of the body.

The third condition necessary to make a process reversible is the *absence of friction*; if there is friction the process is irreversible because work expended on overcoming the friction during expansion is converted into heat and, during the reverse process of contraction the same amount of work must be expended on overcoming friction and converted into heat, i. e., the phenomena are absolutely identical. It will be understood that the presence of friction in a system is connected with a loss of external work, a feature that is, in general, typical of irreversible processes.

Reversible processes are ideal; imparting and extracting heat under real conditions are effected with a finite difference, sometimes very great, in the temperatures of the bodies participating in the transfer of heat; mechanical equilibrium is hardly ever met with and we get vortices in the working body; lastly, every change in the volume of a body is inevitably the cause of friction. Therefore, all actual processes under the conditions obtaining on earth are irreversible.

Equation 2-4 of the first law of thermodynamics

$$dq = du + Adl'$$

is applicable to both reversible and irreversible processes; when applying the equation it must be remembered that dl' is the elementary external work, the work of overcoming external pressure, and that it is effected at the expense of the work of expansion, dl.

In the general case a change in the state of a body is connected with a change in its internal energy and with the work of expansion. In a reversible process the work of expansion dl is expended on overcoming the external pressure, that is,

$$dl = dl'.$$

In the general case of an irreversible process, i. e., when there is friction and mechanical equilibrium does not exist, there will be vortices in the body and the work of expansion, dl, is expended, in addition, on the kinetic energy of the vortices and the work of overcoming friction; giving the symbol dl_r to the sum of these forms of work, we get

$$dl = dl' + dl_r.$$

The work expended on friction and the kinetic energy of the vortices after their subsidence are transformed into an equivalent amount of heat $dq_r = A\, dl_r$; this quantity of heat is usually expended on increasing the internal energy of the body. Therefore, as a result of the irreversibility of a process in which the same amount of heat dq is transmitted to the body, the external work is decreased by dq_r and the internal energy of the body is increased by a like amount.

Since the useful work is equal to the external work, or, more precisely, is proportional to it, and since the increase in the internal energy of the body due to the irreversibility of the process makes it impossible further to obtain equivalent external work, every case of irreversibility leads to a

reduction of the useful work and lowers the efficiency of the process of converting heat into work.

Since, in reversible processes, $dq_r=0$, equation 2-4 for such processes will be written

$$\boxed{dq = du + A\,dl = du + Ap\,dv.} \qquad (2\text{-}8)$$

As we have said, all real processes are irreversible; nevertheless in our further investigations we shall usually examine purely theoretical reversible processes since they are much simpler than irreversible processes; furthermore, in many cases the deviation of actual processes from reversible processes is so small that it may safely be ignored in practical calculations. In cases where the irreversibility of a process greatly changes its character, it will, of course, be taken into account.

Chapter Three

THE HEAT CAPACITY OF A GAS

3-1. The Internal Energy of an Ideal Gas. Since there is no attraction between the molecules of an ideal gas, there can naturally be no internal potential energy but only the kinetic energy of the motion of the molecules (translational energy); the work of dispersion in such a gas is zero. The translational energy of a molecule with a mass m and a velocity w, by equations 1-13 and 1-32, is

$$\frac{mw^2}{2} = aT = \frac{3}{2}kT,$$

where k is the Boltzmann constant.

The translational motion of molecules may be shown graphically in a given direction on a coordinate system of three axes; because of this it is said that the molecules possess three degrees of freedom of translational motion. The basic postulate of the classic kinetic theory is the even distribution of internal energy according to these three degrees of freedom, since this is the most likely distribution, the chaotic movements of the molecules being considered. Each degree of freedom, therefore, corresponds to the internal energy of one molecule, $\frac{1}{2}kT$; for one mol of gas containing N_μ molecules it will be $\frac{1}{2}N_\mu kT$. If there are i degrees of freedom, the internal energy of the mol in heat units will be

$$U_\mu = \mu u = \frac{1}{2}AiN_\mu kT. \qquad (3\text{-}1)$$

But, by equations 1-32 and 1-31

$$N_\mu k = R_\mu = 848.$$

If we give N_μ k this value, and A the value of $\frac{1}{427}$, and substitute in equation 3-1, we get

$$U_\mu = \mu u = \frac{1}{2} \times \frac{1}{427} \times 848iT = 0.9925iT. \qquad (3\text{-}2)$$

The number of degrees of freedom, i, is understood as the number of movements derived from an analysis of the motion of a molecule, or the number of coordinates necessary to define the position of a molecule in space.

The molecule of a monoatomic gas, regarded as a point of matter, possesses only translational motion which can by analysed as three components of direction on the axes of the coordinates. The position of such a molecule is fixed by three coordinates, i. e., for a monoatomic gas the number of degrees of freedom is $i=3$.

The molecule of a diatomic gas, regarded as two rigidly connected points of matter, in addition to its translational motion, may also effect a rotary motion about any axis passing through the molecule's centre of gravity and perpendicular to the line joining the atoms. This rotary motion may be divided into two motions about two perpendicular axes lying in a plane perpendicular to the line joining the atoms and passing through the molecule's axis of rotation. The position of such a molecule is indicated by five coordinates, i. e., the three coordinates of one atom (x_1, y_1, z_1) and two coordinates of the second, (e. g., x_2, y_2), because the third coordinate of the second atom cannot be taken freely but is determined by a simple value from the known geometric relation in space:

$$r = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}$$

where r = the constant distance between the atoms. A diatomic molecule, therefore, possesses three degrees of free translational and two degrees of free rotary motion, i. e., $i=5$.

For a triatomic molecule the rotary motion of the third atom about an axis passing through the first and second atoms is added to the components of the motion of the other two atoms. The position of the third atom is determined by one of its coordinates since the other two coordinates are determined by those of the first and second atoms and by the constant distance of the third atom from the first and second (r_1 and r_2). A triatomic molecule, therefore, has three degrees

of free translational and three degrees of free rotary motion, so that $i=6$ for this molecule.

As far as multiatomic (those having more than three atoms) molecules are concerned, the number of degrees of free motion is obviously the same as that of a triatomic molecule, since the position of a body in space is determined by the positions of three of its points that are rigidly interconnected and do not lie in a straight line; its motions can be analysed as three translational and three rotary.

The above view of molecular structure as a rigid combination of atoms is that of the *classical* kinetic theory of gases; equation 3-2 is based on this theory. According to this equation *the internal energy of an ideal gas* is directly proportional to the number of degrees of free molecular motion; for a given gas it is *a function of the temperature alone*, and is directly proportional to the absolute temperature T. Therefore, *changes in the pressure and volume of an ideal gas that are not accompanied by a change in temperature do not change its internal energy*; with any change of temperature *the change in the internal energy is fully determined for the given gas by the initial and final temperature values, irrespective of the nature of the process.*

According to equation 3-2, when $T=0$ and $u=0$, i. e., at absolute zero, molecular heat motion in an ideal gas ceases; the equation, therefore, gives the value of the internal energy of the gas at a given temperature relative to 0° K. It is, however, usually expressed relatively to 0° C, assuming conventionally the internal energy of the gas to be zero at 0° C; this is a permissible assumption since the study of processes and practical calculations pay attention only to changes in the internal energy and not to its absolute value.

As we shall see later, real gases show a number of deviations from equation 3-2, which was obtained for ideal gases on the basis of the hypothetical postulates of the kinetic theory, no provision being made for the oscillatory motion of the atoms and the forces of molecular attraction.*

3-2. The Weight, Molar and Volume Heat Capacities of Gases. *The weight heat capacity.* If dq units of heat must be

* Recently it has become customary, in determining the internal energy of ideal gases, to take the oscillatory motions of its atoms into consideration. The internal energy and heat capacity, however, are still functions of the temperature alone.

expended to raise the temperature of 1 kg of a body by dt, then the relation

$$c=\frac{dq}{dt} \tag{3-3}$$

is *the specific heat of the body, i. e., the amount of heat required to raise the temperature of 1 kg of the body by 1° C*; it is measured in Calories per kilogram multiplied by degrees (Cal/kg× ×deg). The amount of heat required to raise the temperature of a body weighing G kg by 1° C is called the *heat capacity* of the body; from this it follows that the specific heat is the heat capacity of a body weighing 1 kg; we shall call it *the weight heat capacity.*

We already know that the amount of heat imparted to a body not only depends on temperature changes but also on the conditions under which the heat is transferred, i. e., on the nature of the heating process. The magnitude of the heat capacity also depends on the way in which the temperature is raised by 1° C; when speaking of heat capacity, therefore, the conditions to which reference is being made must be stated.

Using the basic equation 2-10 for reversible processes, we may write

$$c=\frac{dq}{dt}=\frac{du+A\,dl}{dt}=\frac{du}{dt}+\frac{A\,dl}{dt}$$

The second member of the right-hand part is the work of expansion expressed in heat units when the temperature of a body is raised by 1° C; if, by analogy with specific heat, we call this *specific work* and introduce the value

$$h=\frac{A\,dl}{dt}=\frac{Ap\,dv}{dt} \tag{3-4}$$

we get

$$c=\frac{du}{dt}+h. \tag{3-5}$$

The magnitude of the specific work, h, depends on the nature of the process, in view of which the heat capacity per unit weight c may have many values.

In the case of gases there are two special heating processes that are of great importance: (1) the process at constant volume and (2) the process at constant pressure, and the corresponding two values of heat capacity per unit weight, c_v *at constant volume* and c_p *at constant pressure.*

In the first case: $v=\text{const}$, $dv=0$, $dl=p\ dv=0$ so that h is also equal to zero and equation 3-5 becomes

$$c_v=\frac{du}{dt}$$

whence,

$$du=c_v\ dt.$$

As we have already established in Sec. 3-2, the change in the internal energy can be fully determined from the initial and final temperatures; therefore, any change of temperature from t to dt, irrespective of the nature of the process, brings about similar and equal changes in the internal energy:

$$\boxed{du=c_v\ dt,} \tag{3-6}$$

which is the general expression of the elementary change in the internal energy of an ideal gas, although we have obtained it from a particular case in which $v=\text{const}$.

Substituting this value of du in the basic equation 2-8, we get, for the general case of a reversible process in an ideal gas

$$\boxed{dq=c_v\ dt+Ap\ dv,} \tag{3-7}$$

and, making the same substitution in equation 3-5, we get

$$\boxed{c=c_v+h,} \tag{3-8}$$

i. e., the weight heat capacity of an ideal gas is, in the general case, the sum of the weight heat capacity at constant volume and the specific work. It is not difficult to see that equation 3-8 is nothing more than the equation of the first law of thermodynamics applied to reversible processes in which the temperature changes by 1° C; it is obtained from equation 3-7 by dividing it by dt.

The value $\frac{du}{dt}$ in equation 3-5 is identical for all processes while h varies; the value of the weight heat capacity c, therefore, also varies.

If, in particular, a gas changes its state without changing its pressure, we get, by differentiating the equation of state $pv=RT$, with $p=\text{const}$,

$$p\ dv=R\ dT=R\ \ dt$$

[it does not matter whether we write dt or dT because $dT = d(273+t) = dt$], so that in this case the specific work by equation 3-4 is

$$h = \frac{Ap\,dv}{dt} = \frac{AR\,dt}{dt} = AR,$$

and equation 3-8 takes on the form

$$c_p = c_v + AR \tag{3-9}$$

from which it follows that

$$\boxed{c_p - c_v = AR.} \tag{3-10}$$

Since $AR > 0$, then $c_p > c_v$, as can well be understood; to raise the temperature of 1 kg of gas by 1° C it is necessary to expend c_v heat units, which are used exclusively to increase the internal energy of the gas; to raise the temperature of the same body by 1° C when the pressure is constant it is necessary to expend c_p heat units, of which c_v (Cal) are used, as before, to increase the internal energy of the gas, i. e., actually to raise the temperature, and the remainder, $h = c_p - c_v = AR$, is used in carrying out the work of expansion which, in the present case, is connected with the increase in temperature, as follows from the equation of state. Thus we see that the *gas constant R is the specific work of a gas at constant pressure*, i. e., the work of expansion of 1 kg of gas in kilogram-metres when the temperature is raised by 1° C and the pressure is constant; in conformity with this its unit of measure is kgm/kg × degrees as we established in Sec. 1-5.

Therefore, the difference between the weight heat capacities at constant pressure and constant volume, c_p and c_v, for a given gas, according to equation $pv = RT$, is a constant value, so that to determine the values of c_p and c_v for different gases it is only necessary to find the value of one of them experimentally. It is difficult to find the weight heat capacity c_v by direct experimentation because the weight of the gas is very small as compared with that of the container and it is not easy to obtain an accurate result. The majority of experiments consist in determining the value of c_p.

Table 3-1 gives the values of c_p and c_v obtained experimentally at temperatures between 15° and 20°C for the chief technical gases, and also the values of the gas constant R, the molecular weight μ, and the specific weight γ_0 at STP.

Table 3-1

Gas	Chemical formula	Atoms in 1 molecule	Molecular weight (μ)	Specific weight (γ_0) at STP	Gas constant (R)	Weight heat capacities	
						c_p	c_v
Oxygen	O_2	2	32	1.429	26.5	0.218	0.156
Hydrogen	H_2	2	2.016	0.09	420.6	3.405	2.42
Nitrogen	N_2	2	28.02	1.251	30.26	0.249	0.178
Carbon monoxide	CO	2	28	1.250	30.29	0.250	0.179
Air	—	(2)	(29)	1.293	29.27	0.240	0.172
Carbon dioxide	CO_2	3	44	1.963	19.28	0.202	0.157
Acetylene	C_2H_2	4	26.016	1.16	32.6	0.370	0.294
Methane	CH_4	5	16.032	0.715	52.9	0.518	0.394
Ethylene	C_2H_4	6	28.032	1.25	30.25	0.361	0.290

Molar heat capacity of a gas. Let c be the weight heat capacity and μ the molecular weight of a gas; the product μc is then obviously the heat capacity of 1 mol of gas, known as the *molar heat capacity*, measured in Cal/mol × degrees.

Molar heat capacity, similar to weight heat capacity, has two values, μc_p at constant pressure, and μc_v at constant volume.

The difference in the molar heat capacities of an ideal gas is

$$\mu c_p - \mu c_v = \mu (c_p - c_v) = \mu AR, \qquad (3\text{-}11)$$

but since equation 1-31 states that $\mu R = 848$ for all ideal gases

$$\mu c_p - \mu c_v = \mu AR = \frac{848}{427} = 1.985 \approx 2, \qquad (3\text{-}12)$$

and, consequently,

$$c_p - c_v = \frac{1.985}{\mu} \approx \frac{2}{\mu}. \qquad (3\text{-}13)$$

Thus the difference in the molar heat capacities μc_p and μc_v is a constant value identical for all ideal gases

Differentiating equation 3-2

$$\mu u = 0.9925\, iT,$$

which we derived from the basic postulate of the kinetic theory, we get

$$\mu\, du = 0.9925\, i\, dt;$$

substituting $du = c_v\,dt$ (from equation 3-6) we get

$$\mu c_v\,dt = 0.9925\,i\,dt$$

from which it follows that

$$\mu c_v = 0.9925\,i \approx i, \qquad (3\text{-}14)$$

i. e., the molar heat capacity μc_v and, consequently, $\mu c_p = \mu c_v + 1.985$, are identical for all ideal gases with a similar number of degrees of freedom and are constant values and, furthermore, μc_v in Calories is approximately equal to the number of degrees of freedom i, and $\mu c_p \approx i + 2$.

In particular, according to equations 3-14 and 3-12, $i = 3$ for monoatomic gases

$$\mu c_v = 0.9925 \times 3 = 2.9775 \approx 3$$

and

$$\mu c_p = 2.9775 + 1.985 = 4.9625 \approx 5$$

which agrees fairly well with experimental data; it has been found by experimentation that $\mu c_p = 4.989$ for helium and 4.917 for argon.

For diatomic gases ($i = 5$)

$$\mu c_v = 0.9925 \times 5 = 4.9625 \approx 5$$

and

$$\mu c_p = 4.9625 + 1.985 = 6.9475 \approx 7;$$

by direct experimentation the following data have been obtained for temperatures between 15° and 20° C:

	O_2	H_2	N_2	CO	Air	
$\mu c_p =$	6.98	6.85	6.99	6.99	6.96	Cal/mol × degrees.

As we see from this table, practical experiments agree fairly closely with theory as far as diatomic gases within these temperature limits are concerned.

For triatomic and multiatomic gases ($i = 6$),

$$\mu c_v = 0.9925 \times 6 = 5.955 \approx 6$$

and

$$\mu c_p = 5.955 + 1.985 = 7.94 \approx 8;$$

by experiment the following values have been found for the superheated vapours of carbon dioxide and water (triatomic gases) and for acetylene (C_2H_2 — four atoms), methane (CH_4—

five atoms) and for ethylene (C_2H_4—six atoms)

	CO_2	H_2O	C_2H_2	CH_4	C_2H_4	
$\mu c_p =$	8.89	8.19	9.62	8.3	10.1	Cal/mol × degrees

Thus we see that for these gases the divergence from the theoretical values is substantial, especially for acetylene and ethylene which gives us reason to believe that the postulates of the classical kinetic theory are not quite correct for the multiatomic gases. It stands to reason that in making practical calculations the experimental figures should be used.

The volume heat capacity of a gas. If c is the weight heat capacity of a gas, and γ is the specific weight, then obviously

$$C = \gamma c$$

is the heat capacity of 1 cum of gas; this we shall call the *volume heat capacity*; it is measured in Cal/cum × deg. It will be seen that volume heat capacity may also be obtained by dividing the molar heat capacity μc, by the volume of the mol, μv, i. e.,

$$\frac{\mu c}{\mu v} = \frac{c}{v} = \gamma c = C.$$

The specific weight of a gas and the volume of the mol, however, are variables that depend on temperature and pressure; it is, therefore, necessary to state the temperature and pressure at which 1 cum of gas is taken when determining the volume heat capacity; usually STP is taken for the calculation. At STP the volume of the mol is $\mu v = 22.4$ cum; therefore,

$$C = \frac{\mu c}{22.4} \frac{\text{Cal}}{\text{cumn} \times \text{deg}}$$

where cumn is the so-called "*normal cubic metre*", that is, a cubic metre at 0°C and 760 mm Hg. It must be thoroughly understood that STP, in this case, refers to the cubic metre of gas and not to the heat capacity C.*

Volume heat capacity has two values, C_p when pressure is constant and C_v when volume is constant similar to the c_p and c_v which we distinguished for weight heat capacity. The difference between them,

$$C_p - C_v = \gamma c_p - \gamma c_v = \gamma (c_p - c_v) = \gamma AR, \qquad (3\text{-}15)$$

* Since a cubic metre of the given gas at STP contains a fully defined weight of that gas, the so-called volume heat capacity also refers to a fully defined weight of gas.—*Ed.*

depends, as we see, on γ, that is, on the conditions under which 1 cum of the gas is taken, because γ depends on temperature and pressure, so that at STP

$$C_p - C_v = \frac{\mu c_p - \mu c_v}{22.4} = \frac{1.985}{22.4} = 0.0886. \qquad (3\text{-}16)$$

The volume heat capacity of gases with identical molar heat capacities will, obviously, also be identical.

All three methods of computing heat capacity are used in engineering, depending on circumstances.

3-3. The Dependence of the Heat Capacity of a Gas on Temperature. True and Mean Heat Capacity. According to the classical kinetic theory, the weight heat capacities of any ideal gas, c_p and c_v, are constant values. Experiments have shown that for diatomic and multiatomic gases they depend on temperature and pressure, although the latter dependence is so insignificant where the more perfect gases are concerned that it is usually ignored.

The general phenomenon is that the weight heat capacities c_p and c_v increase as temperature increases.

Until recently it was assumed, on the basis of available experimental data, that the dependence of c_p and c_v on temperature, in the case of the more perfect gases, in particular the diatomic gases, could be expressed by the straight-line equations

$$c_p = a_p + bt \text{ and } c_v = a_v + bt, \qquad (3\text{-}17)$$

where a_p, a_v and b are constants for the given gas; in these expressions the coefficient of t is the same (b), because for a gas that obeys the equation $pv=RT$ the difference $c_p - c_v = AR$ is a constant value for the given gas; consequently, it is also true that $a_p - a_v = AR$.

In this case the molar heat capacities μc_p and μc_v and the volume heat capacities C_p and C_v should also be expressible by similar straight-line equations since they are both multiples of the weight heat capacities c_p and c_v.

More recent experimental work, however, has shown that the dependence of heat capacity on temperature is a more complex relation and has a specific character for each individual gas; nevertheless, the assumption that these straight-line equations are true enough for a number of gases within a limited range of temperatures will provide an approxima-

tion sufficiently accurate for practical purposes. For diatomic gases, for instance, the following is fairly accurate at temperatures up to 1000° C

$$\left.\begin{aligned} \mu c_p &= 6.69 + 0.000532\,t; \\ \mu c_v &= 4.995 + 0.000532\,t. \end{aligned}\right\} \qquad (3\text{-}18)$$

The values of the heat capacities of O_2, N_2, CO and air, obtained by equation 3-18, agree well enough with the experimentally obtained values within the above temperature range, but for hydrogen the figures are somewhat high. As far as gaseous carbonic acids, superheated steam and multiatomic gases in general are concerned, the dependence of their heat capacities on temperature cannot be satisfactorily explained by a straight-line equation. For practicalcal culations, therefore, it is advisable to use the detailed tables compiled from experimental data (see appendices).

The variability of heat capacity due to temperature changes has a greater effect on calculations the greater the change; if the change is small it is often permissible to assume that heat capacity for the given process is a constant. This greatly simplifies the calculation, as will be apparent later.

The classic kinetic theory that assumes the even distribution of the internal energy by degrees of freedom and also the rigid combination of atoms in molecules, is unable to explain either the dependence of heat capacity on temperature or the difference in the molar heat capacities of gases with similar degrees of freedom. It is possible to explain it if we reject the concept of the molecule as a rigid combination of atoms, and assume, as modern molecular physics do, that in addition to the translational and rotational motions there is also an oscillatory motion of atoms within the molecule itself; this gives the atoms kinetic and potential energy, the so-called *intramolecular energy*, which does not enter into classic theory.

An exhaustive explanation of the properties of real gases, insofar as they concern heat capacity, is given by *the quantum theory of heat capacity*. This theory has recently been elaborated on the basis of the general *quantum theory* (see any modern manual of physics) and takes account of the oscillatory motion of atoms.

The existence of intramolecular atomic oscillations increases the number of degrees of freedom by the number of axes joining the centres of the atoms, i. e., for diatomic gases

the number increases from five to six, for triatomic—from six to nine, for tetratomic—from six to twelve, with a consequent increase in the internal energy of the gas which is the greater the more complicated its molecules. It is the existence of these oscillations that conditions the dependence of heat capacity on temperature, again, the greater the more complicated the molecules.

True and mean heat capacity. From the basic equation defining weight heat capacity (equation 3-3)

$$c = \frac{dq}{dt}$$

we get

$$dq = c\,dt \tag{3-19}$$

and, consequently, for the general case of a change in temperature from t_1 to t_2

$$q = \int_{t_1}^{t_2} c\,dt. \tag{3-20}$$

This last equation enables us to determine the amount of heat imparted to or taken from a gas by the change of temperature alone, provided the functional relation of c and t is known. If we assume that c is constant, then

$$q = c\,(t_2 - t_1);$$

in reality the heat capacity changes with the temperature so that every value of t has a corresponding value of c, which is known as the *true heat capacity* at the given temperature.

If the heat capacity, within the given temperature limits, changes in accordance with the straight-line law

$$c = a + bt,$$

then we get from equation 3-20

$$q = \int_{t_1}^{t_2} c\,dt = \int_{t_1}^{t_2} (a + bt)\,dt = a\,(t_2 - t_1) + b\,\frac{t_2^2 - t_1^2}{2} =$$

$$= \left(a + b\,\frac{t_1 + t_2}{2}\right)(t_2 - t_1) = (a + bt_m)\,(t_2 - t_1) =$$

$$= c_m\,(t_2 - t_1), \tag{3-21}$$

where $t_m = \frac{t_1+t_2}{2}$ is the mean temperature of the process equal to half the sum of the end temperatures;

$c_m = a + bt_m$ is *the mean weight heat capacity of the process*, corresponding to the mean temperature of the process t_m and therefore equal to half the sum of the true heat capacities $c_1 = a + bt_1$ and $c_2 = a + bt_2$ at the beginning and end of the process.

It is, therefore, sufficient in the given case to determine $t_m = \frac{t_1 + t_2}{2}$ and by using it determine the mean weight heat capacity c_m; the amount of heat q is obtained by the simple relation

$$q = c_m (t_2 - t_1).$$

We know, however, that the dependence of c from t is of a more intricate nature; nevertheless the amount of heat q is quite easily determined from the tables of mean heat capacity c_m for the range of temperatures from 0 to t °C which are obtained in the following way.

Let it be assumed that the curve ab (Fig. 3-1) shows the dependence of weight heat capacity on temperature, $c = f(t)$;

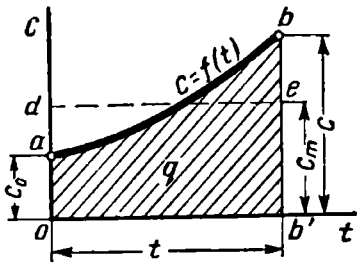


Fig. 3-1

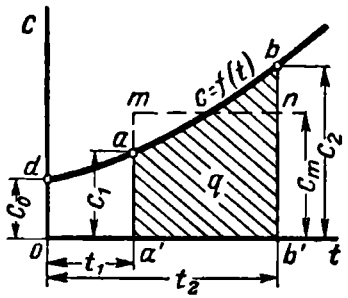


Fig. 3-2

in the given case the quantity of heat, q, necessary to raise the temperature from 0° C to t° C, according to equation 3-20, is $q = \int_0^t c\,dt$ and is equal to area $abb'o$ below the curve ab. The weight heat capacity changes from c_0 at 0°C to c at t° C; on the average, the amount of heat expended on raising

the temperature by 1° C within these limits is

$$c_m = \frac{q}{t} = \frac{\text{area } abb'o}{ob'}$$

which is known as *the mean weight heat capacity within the limits* 0°-t° C. In practice c_m is obtained as the height of a rectangle *deb'o*, equal in area to *abb'o*, and is derived planimetrically therefrom, and divided by its base *ob'*. With c_m a known quantity,

$$q = c_m t. \tag{3-22}$$

Using the tables to find the value of c_m, the amount of heat, q, imparted to the gas in raising the temperature from t_1 to t_2 (Fig. 3-2) is found as follows. The amount of heat, q, according to equation 3-20, is

$$q = \int_{t_1}^{t_2} c\,dt$$

and is measured as area *abb'a'* which may be regarded as the difference in the areas of the two figures

$$\text{area } abb'a' = \text{area } dbb'o - \text{area } daa'o.$$

Area *daa'o* gives the amount of heat, q_1, consumed in raising the temperature from 0° to t_1°C, which, by equation 3-22, is

$$q_1 = c_{m_1} t_1,$$

where c_{m_1} is the average heat capacity from 0° to t_1°C. Similarly, area *dbb'o* gives the amount of heat, q_2, expended on raising the temperature from 0° to t_2°C, and is expressed by

$$q_2 = c_{m_2} t_2,$$

where c_{m_2} is the average heat capacity from 0° to t_2°C. In the latter case

$$q = q_2 - q_1 = c_{m_2} t_2 - c_{m_1} t_1, \tag{3-23}$$

i. e., the calculation is simply one of multiplying the two figures for average heat capacity (obtained from the tables) by the relevant temperatures and subtracting the product of one from the product of the other.

The average weight heat capacity for the process *ab*, i. e., where the end temperatures are t_1 and t_2, is

$$c_m = \frac{q}{t_2 - t_1} = \frac{c_{m_2} t_2 - c_{m_1} t_1}{t_2 - t_1};$$

obviously this average will be equal to the height of the rectangle *mnb'a'* which is equal in area to *abb'a'*. It is easy to see that only when the dependence of c on the temperature is graphically a straight line does $c_m = \frac{c_1 + c_2}{2}$ where c_1 and c_2 are the true initial and final heat capacities.

All that has been said is equally true of the volume and molar heat capacities.

In the appendices to this book there are detailed tables of heat capacities $(\mu c_p)_m$ and c_{p_m} for oxygen, nitrogen, hydrogen, carbon monoxide, air and also gaseous carbonic acids and superheated steam between the limits 0° and 3000° C which were compiled in 1945 by M. P. Vukalovich and V. A. Kirillin.

Using these tables, the values of heat capacities when volume is constant may be obtained from the equations

$$(\mu c_v)_m = (\mu c_p)_m - 1.985;$$
$$c_{v_m} = c_{p_m} - AR.$$

The heat capacity of a gaseous mixture. If the composition of the gas is given by the weight of the various gases of which it is composed, $g_1, g_2, \ldots, g_n$, then the weight heat capacity will obviously be

$$c = g_1 c_1 + g_2 c_2 + \ldots + g_n c_n \qquad (3\text{-}24)$$

where $c_1, c_2, \ldots, c_n$ are the weight heat capacities of the component gases. If the composition is given by volume, $r_1, r_2, \ldots, r_n$, then it is more expedient to find the heat capacity by volume, i. e.,

$$C = r_1 C_1 + r_2 C_2 + \ldots + r_n C_n \qquad (3\text{-}25)$$

where $C_1, C_2, \ldots, C_n$ are the heat capacities by volume of the various gases, or the molar heat capacity

$$\mu c = r_1 \mu_1 c_1 + r_2 \mu_2 c_2 + \ldots + r_n \mu_n c_n \qquad (3\text{-}26)$$

where $\mu_1 c_1$, $\mu_2 c_2$, ..., $\mu_n c_n$ are the molar heat capacities of the component gases.

Actually, equations 3-25 and 3-26 are the same, the only difference being that equation 3-25 is for 1 normal cum of the mixture and 3-26 for the volume of 1 mol, i. e., the second equation is obtained by multiplying the first by the volume of the mol, the same for all gases under normal conditions, $\mu v = 22.4$ normal cum.

Example 3-1. Determine the average molar, volume and weight heat capacities of generator gas, pressure and volume being constant at 200° C, the mixture consisting of 18% H_2, 24% CO, 6% CO_2 and 52% N_2 (example 1-9, Sec. 1-6).

Using the tables in the appendix and substituting in equation 3-26, we get

$$(\mu c_p)_m = 0.18 \times 6.9 + 0.24 \times 7.08 + 0.06 \times 9.581 + \\ + 0.52 \times 7.01 = 7.169 \text{ Cal/mole} \times \text{degrees}$$

and according to equation 3-12

$$(\mu c_v)_m = (\mu c_p)_m - 1.985 = 7.169 - 1.985 = 5.184 \text{ Cal/mole} \times \text{degrees}.$$

The volume heat capacities reduced to 1 normal cum of gas

$$C_{p_m} = \frac{7.169}{22.4} = 0.32 \text{ Cal/cumn} \times \text{deg}.$$

and

$$C_{v_m} = \frac{5.184}{22.4} = 0.231 \text{ Cal/cumn} \times \text{deg}.$$

Since the specific weight of the gas under these conditions was determined earlier in this book as being $\gamma = 1.085$ kg-cumn, the weight heat capacity will be

$$c_{p_m} = \frac{C_{p_m}}{\gamma} = \frac{0.32}{1.085} = 0.295 \text{ Cal/kg} \times \text{deg}.$$

$$c_{v_m} = \frac{C_{v_m}}{\gamma} = \frac{0.231}{1.085} = 0.213 \text{ Cal/kg} \times \text{deg}.$$

3-4. The Relation of the Heat Capacities of a Gas at Constant Pressure and at Constant Volume. In thermodynamics an important part is played by the relation of the heat capacities:

$$k = \frac{c_p}{c_v} = \frac{\mu c_p}{\mu c_v} = \frac{C_p}{C_v}. \qquad (3\text{-}27)$$

According to deductions made from the classic kinetic theory (equations 3-14 and 3-12)

$$\mu c_v = 0.9925\, i \text{ and } \mu c_p = \mu c_v + 1.985 = 0.9925\, i + 1.985$$

where i is the number of degrees of freedom of the molecules and, consequently,

$$k = 1 + \frac{2}{i}, \tag{3-28}$$

i. e., the relation k is fully determined by the degrees of freedom of the molecules and is the smaller, the more complicated the molecule.

Equation 3-28 shows, in particular, that

for monoatomic gases ($i=3$) $k = \frac{5}{3} = 1.667$;

for diatomic gases ($i=5$) $k = \frac{7}{5} = 1.4$;

for triatomic gases ($i=6$) $k = \frac{3}{4} = 1.333$.

These purely theoretical figures accord quite well with experimentally obtained data: for monoatomic argon exactly the same figure, $k=1.667$ has been obtained; for diatomic gases at room temperature:

Air	CO	O_2	H_2	N_2
$k=1.4$	1.401	1.398	1.408	1.41

and for triatomic gases at the same room temperature

H_2O	CO_2
$k=1.33$	1.305

We have seen, however, that in reality the heat capacities c_p and c_v are not constant for the given gas, but vary with temperature; from this it follows that $k = \frac{c_p}{c_v}$ must also be a function of the temperature. Applying equation 3-9 we may write

$$k = \frac{c_p}{c_v} = \frac{c_v + AR}{c_v} = 1 + \frac{AR}{c_v} \tag{3-29}$$

because c_v increases as temperature increases and k is simultaneously reduced. The approximation for diatomic gases is

$$k = 1.4 - 0.00005\, t. \tag{3-30}$$

The weight heat capacities c_p and c_v may by expressed by k; actually, from equation 3-29

$$c_v = \frac{AR}{k-1} \tag{3-31}$$

and, consequently,

$$c_p = \frac{k}{k-1} AR. \tag{3-32}$$

Molar heat capacities are similarly expressed:

$$\mu c_v = \frac{\mu AR}{k-1} = \frac{1.985}{k-1}; \tag{3-33}$$

$$\mu c_p = 1.985 \frac{k}{k-1}. \tag{3-34}$$

Since the value of k can be obtained experimentally, it may be used to find the value of the heat capacities by a simple calculation employing equations 3-31 and 3-34 (do not confuse $k = \frac{c_p}{c_v}$, which is greater than 1, with the Boltzmann constant $k = \frac{848}{N_\mu} = 1.37 \times 10^{-16}$ erg/deg).

3-5. Enthalpy (Heat Content) of a Gas. Substituting in the basic equation for reversible processes

$$dq = du + Ap\ dv;$$
$$p\,dv = d(pv) - v\,dp$$

we get

$$dq = du + Ad(pv) - Av\ dp = d(u + Apv) - Av\ dp,$$

and introducing the value

$$\boxed{i = u + Apv} \tag{3-35}$$

we get

$$\boxed{dq = di - Av\,dp.} \tag{3-36}$$

The magnitude i, which, according to equation 3-35, is determined by the internal energy of the body, its specific pressure and specific volume, is obviously a function of the state of the body, so that di is the full differential of that function. It follows, therefore, that the value i, similarly to p, v, t, and u describes the state of the body, i. e., all of them are parameters of the state of the body. It is fairly easy to get some idea of its physical significance; in fact, when p is constant, equation 3-36 may be expressed thus:

$$dq_p = di, \tag{3-37}$$

in other words, di is the elementary amount of heat imparted to a body under constant pressure. The magnitude i is called the *enthalpy* or *heat content at constant pressure*. The term "heat content" is mostly used in Russia, but we do not regard it as suitable and shall employ the term "enthalpy" which is now gaining greater recognition.

The introduction of the magnitude i greatly simplifies many thermodynamic calculations, especially where vapours are concerned; obviously it has great practical significance.

For an ideal gas

$$di = d\,(u + Apv) = du + Ad\,(pv) = c_v dT + Ad\,(RT) = \\ = c_v dT + AR\,dT = (c_v + AR)\,dT = c_p dT,^* \qquad (3\text{-}38)$$

which, incidentally, could have been evolved directly from the very concept of enthalpy.

Calculations involving the enthalpy of a gas i may be made from 0° K or 0° C; in the first case

$$i = \int_0^T c_p\,dT = c_{p_m} T;$$

in the second case

$$i' = \int_0^t c_p\,dt = c'_{p_m} t$$

where c_{p_m} is the mean heat capacity from 0° to T° K and c'_{p_m} is the mean heat capacity from 0° to t° C. The values of i and i' are, of course, different, but this is of no significance to the calculations since it is the change in enthalpy that is of practical interest and not its absolute value. The change in the enthalpy of a gas in a finite process

$$i_2 - i_1 = \int_{T_1}^{T_2} c_p dT = c_{p_{m_2}} T_2 - c_{p_{m_1}} T_1$$

and

$$i'_2 - i'_1 = \int_{t_1}^{t_2} c_p dt = c'_{p_{m_2}} t_2 - c'_{p_{m_1}} t_1,$$

both methods of calculation being identical.

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* $di = d\,(u + Apv) = du + Ad\,(pv) = c_p dT$ is true for all substances and not only for ideal gases.—*Ed.*

Chapter Four

GAS PROCESSES

4-1. The Study of Gas Processes. In the most general case of a change of state, heat is imparted to or taken from a gas, the pressure, volume and temperature of which change simultaneously. The study of the process involves the determination of the work, l, done by the gas, the change in the internal energy (u_2-u_1), the amount of heat, q, the weight heat capacity, c, and the establishment of the connection between the separate values that describe the state of a gas. However, it is not the general, completely arbitrary process that possesses practical interest, but the special cases, those that play an important role in heat engineering. The special processes that are of greatest importance, both theoretically and practically, are:

1. A process in which the volume is constant (v=const) known as the *isochoric process.*
2. A process in which the pressure is constant (p=const) known as the *isobaric process.*
3. A process in which the temperature is constant (t= =const) known as the *isothermic process.*
4. A process in which there is no exchange of heat (dq=0) known as the *adiabatic process.*
5. A process in which the equation of the pressure curve pv^n=const, where n is, in turn, a constant value for the given process; this is known as the *polytropic process*; as we shall see later, the first four processes, may, in certain instances, be regarded as particular cases of polytropic change.

The investigation of these processes, assuming them to be reversible, will consist in applying the basic relations for ideal gases:

$$dq = du + Adl = c_v dt + Ap\,dv;$$
$$dq = c\,dt;$$
$$pv = RT,$$

and their gaphic representation in a pv diagram is of value to us because it gives the work, l, done by the gas as the area below the curve. We shall, therefore, be investigating the reversible processes of ideal gases, that is, processes that are purely theoretical. Real processes will, of course, show a number of deviations from the theoretical, although in many cases they are not significant.

4-2. The Isochoric Process. It follows from the equation $pv=RT$ when $v=$const, that

$$\frac{p}{T}=\frac{R}{v}=\text{const}, \tag{4-1}$$

that is, *the pressure of the gas is directly proportional to its absolute temperature*, and, consequently,

$$\frac{p_2}{p_1}=\frac{T_2}{T_1}. \tag{4-2}$$

When $v=$const, $dv=0$ and $dl=p\ dv=0$, i. e., when no work is performed, the basic equation may be written very simply:

$$dq=du=c_v dt;$$

all the heat imparted to the gas goes towards increasing its internal energy, i. e., actually to raising its temperature, which is connected with increased pressure. The weight heat capacity of the process is $c=c_v$ and the specific work, $h=0$.

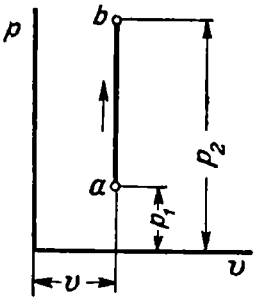


Fig. 4-1

For a finite process where c_v is variable

$$q=u_2-u_1=c_{v_{m_2}}t_2-c_{v_{m_1}}t_1, \tag{4-3}$$

where c_{vm1} and c_{vm2} are the mean heat capacities when there is a constant volumé within the range of 0 to t_1 and t_2° C.

When c_v is constant

$$q=u_2-u_1=c_v(t_2-t_1). \tag{4-4}$$

The line of the process, the *isochor*, in the system pv is a section of the vertical straight line ab (Fig. 4-1). In the direction indicated by the arrow, we have a process due to heat imparted to the gas (heating) because the pressure increases and, consequently, according to equation 4-2, the temperature

is also increased. An increase in the temperature of a gas means an increase in its internal energy which, in the present process, is obtained from the heat, q, imparted to the gas from outside.

Example 4-1. Air is contained in a reservoir of 30 litres capacity at a pressure of 2 ata and a temperature of 30° C. What quantity of heat must be imparted to the air to raise its pressure to 4 ata?

According to equation 4-2 the final temperature of the air will be

$$T_2 = T_1 \frac{p_2}{p_1} = 303 \times \frac{4}{2} = 606° \text{ K}$$

and

$$t_2 = 606 - 273 = 333° \text{ C}.$$

From the tables in the appendix we find by interpolation that

$$c_{p_{m_2}} = 0.243 + \frac{0.246 - 0.243}{100} \times 33 = 0.244;$$

$$c_{p_{m_1}} = 0.24.$$

Since, for air, $AR = \frac{29.27}{427} = 0.068$,

$$c_{v_{m_1}} = 0.24 - 0.068 = 0.172 \text{ Cal/kg} \times \text{deg}$$
$$c_{v_{m_2}} = 0.244 - 0.068 = 0.176 \text{ Cal/kg} \times \text{deg}.$$

Applying equation 4-3

$$q = 0.176 \times 333 - 0.172 \times 30 = 53.44 \text{ Cal/kg}.$$

From the equation of state $pV = GRT$ we get the weight of the air

$$G = \frac{p_1 V}{RT_1} = \frac{20{,}000 \times 0.03}{29.27 \times 303} = 0.0676 \text{ kg}$$

and the amount of heat imparted to it is

$$Q = Gq = 0.0676 \times 53.44 = 3.1 \text{ Cal}.$$

4-3. The Isobaric Process. From the equation of state $pv = RT$ when p is constant, it follows that

$$\frac{v}{T} = \frac{R}{p} = \text{const}, \qquad (4\text{-}5)$$

i. e., the volume of the gas is directly proportional to its absolute temperature, since, when there is expansion at constant pressure, the temperature of the gas, and, consequently, *its internal energy, increase*; when there is compression they decrease.

The relation

$$\frac{v_2}{v_1} = \frac{T_2}{T_1} \tag{4-6}$$

follows from equation 4-5.

The work performed is

$$l = \int_{v_1}^{v_2} p\,dv = p \int_{v_1}^{v_2} dv = p\,(v_2 - v_1), \tag{4-7}$$

and since

$$pv_1 = RT_1 \text{ and } pv_2 = RT_2,$$

simultaneously

$$l = R\,(T_2 - T_1) = R\,(t_2 - t_1). \tag{4-8}$$

The weight heat capacity of the process is $c = c_p$ so that, in connection with equation 3-38

$$dq = c_p dt = di$$

and, consequently, by equation 3-23

$$q = \int_{t_1}^{t_2} c_p dt = c_{p_{m_2}} t_2 - c_{p_{m_1}} t_1 = i_2 - i_1, \tag{4-9}$$

where $c_{p_{m_1}}$ and $c_{p_{m_2}}$ are mean heat capacities with pressure constant between the limits 0° to t_1 and t_2 °C.

When $c_p = \text{const}$, we have a simpler expression

$$q = c_p\,(t_2 - t_1). \tag{4-10}$$

The change in the internal energy is

$$u_2 - u_1 = \int_{t_1}^{t_2} c_v dt = c_{v_{m_2}} t_2 - c_{v_{m_1}} t_1, \tag{4-11}$$

where $c_{v_{m_1}}$ and $c_{v_{m_2}}$ are the average heat capacities with pressure constant within the range of 0° to t_1 and t_2 °C.

When $c_v = \text{const}$

$$u_2 - u_1 = c_v\,(t_2 - t_1). \tag{4-12}$$

The specific work of the process is $h = c_p - c_v = AR$.

The line of the process, the *isobar*, in the *pv* system is a section of the horizontal straight line *ab* (Fig. 4-2). The area of the rectangle *abb'a'* gives the value, on a certain scale, of the work, *l*, performed by the gas. In the direction indicated by the arrow, the process is one of imparting heat to the gas (heating) because, as we have established above, isobaric expansion is accompanied by an increase in temperature and, consequently, by an increase in the internal energy, which, similarly to the work done, requires the transfer of heat from outside.

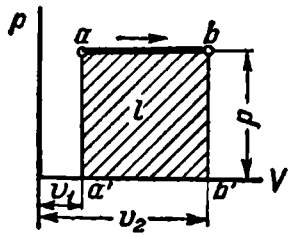


Fig. 4-2

It can easily be seen that in an isobaric gas process $Al<q$, because in isobaric expansion the heat q is expended on increasing the internal energy (u_2-u_1) and on the work of expansion, l.

If we divide the basic equation $dq=du+A\,dl$ by dq we get

$$\frac{du}{dq}+\frac{A\,dl}{dq}=1,$$

whence

$$\frac{A\,dl}{dq}=1-\frac{du}{dq}.$$

The relation $\frac{A\,dl}{dq}$ determines that part of the total amount of heat dq which is converted into the work of expansion, dl. Substituting in this equation $du=c_v dt$ and $dq=c_p dt$ we get the following for the isobaric process:

$$\frac{A\,dl}{dq}=1-\frac{c_v\,dt}{c_p\,dt}=1-\frac{c_v}{c_p}=1-\frac{1}{k}.$$

Assuming that $k=1.4$ for diatomic gases,

$$\frac{A\,dl}{dq}=1-\frac{1}{1.4}=0.285,$$

that is, only 28.5% of the heat imparted to the gas is expended on the work of expansion and 71.5% on increasing the internal energy, i.e., on raising the temperature.

Example 4-2. How much heat per hour must be imparted to the air circulating in an air heating system if its temperature has to be raised from $-10°$ to $+50°$ C and the hourly consumption of warm air is 1,200 cum per hour at a pressure of 760 mm Hg?

The process takes place at constant (atmospheric) pressure so that in this case, in view of the low temperatures, it is permissible to assume c_p constant and equal to 0.24.

Each kilogram of air, on being heated, acquires the following amount of heat

$$q = c_p (t_2 - t_1) = 0.24 (50 + 10) = 14.4 \text{ Cal/kg.}$$

The consumption of air, by weight, per hour

$$G = \gamma_2 V_2$$

where V_2 = the consumption of air by volume at 50° C, 760 mm Hg;

γ_2 = the specific weight under the same conditions.

From equation of state $pv = RT$

$$\gamma_2 = \frac{1}{v_2} = \frac{p}{RT_2} = \frac{10{,}333}{29.27 (273 + 50)} = 1.09 \text{ kg-cum}$$

so that

$$G = 1.09 \times 1{,}200 = 1{,}310 \text{ kg/hr.}$$

The hourly consumption of heat, therefore, is

$$Q = Gq = 1{,}310 \times 14.4 = 18{,}850 \text{ Cal. p. h.}$$

Example 4-3. Two kilograms of dry air* at a temperature of 30° C expands at constant pressure to a volume 1.4 times greater than the initial volume. Determine the final temperature, the work of expansion and the amount of heat expended.

According to equation 4-6

$$T_2 = T_1 \frac{v_2}{v_1} = 303 \times 1.4 = 424° \text{ K}$$

and

$$t_2 = 424 - 273 = 151° \text{ C,}$$

the work, by equation 4-8, is

$$L = 2l = 2 \times 29.27 (151 - 30) = 7{,}100 \text{ kgm.}$$

Assuming for this case that $c_p = 0.24$ we get the amount of heat

$$Q = 2q = 2 \times 0.24 (151 - 30) = 58 \text{ Cal.}$$

It is of interest to note that in this example the solution does not require a knowledge of the constant pressure of the air, since the values of T_2, L and Q are the same for all values of the pressure p under the given conditions.

4-4. The Isothermic Process. When t=const,

$$pv = RT = \text{const.} \qquad (4\text{-}13)$$

This is the analytical expression of the Boyle-Mariotte law (equation 1-16) and is also the equation of the curve of the

* That is, air which does not contain water vapour.—*Ed.*

process, the *isotherm* in the *pv* system, an equilateral hyperbola, the axes of whose coordinates are asymptotes.

It follows from equation 4-13 that the pressure and the volume are inversely proportional to each other so that in isothermic expansion the pressure of the gas is reduced and in compression it increases. We can, therefore, write

$$\frac{p_2}{p_1} = \frac{v_1}{v_2}. \tag{4-14}$$

When $t = \text{const}$, $dt = 0$, and, consequently,

$$du = c_v\, dt = 0;$$
$$di = c_p\, dt = 0,$$

i. e.,

$$\underline{u = \text{const}}, \text{ and } \underline{i = \text{const}}, \tag{4-15}$$

so that *a process at constant temperature is, for ideal gases, also a process at constant internal energy (isodynamic) and at constant enthalpy.*

The basic equation is very simple:

$$dq = A\, dl = Ap\, dv,$$

i. e., all the heat imparted to the gas is converted into the work of expansion; consequently, in cases of isothermic compression the amount of heat taken from the gas must be equal to the work expended from outside on compression.

The work

$$l = \int_{v_1}^{v_2} p\, dv = \int_{v_1}^{v_2} \frac{RT}{v}\, dv = RT \int_{v_1}^{v_2} \frac{dv}{v} = RT \ln \frac{v_2}{v_1} =$$
$$= RT \ln \frac{p_1}{p_2} = p_1 v_1 \ln \frac{v_2}{v_1} = p_1 v_1 \ln \frac{p_1}{p_2}. \tag{4-16}$$

The amount of heat

$$q = Al = ART \ln \frac{v_2}{v_1} = ART \ln \frac{p_1}{p_2} = Ap_1 v_1 \ln \frac{v_2}{v_1} =$$
$$= Ap_1 v_1 \ln \frac{p_1}{p_2}. \tag{4-17}$$

Fig. 4-3 is the graphic representation of the isothermic expansion process of an ideal gas in the system *pv*. As we have said, it is represented by the section *ab* of an equilateral hyperbola; area *abb'a'* below the curve gives, in the present

case, both the value of l, the work of the gas, and of q, the heat imparted to the gas (in units of work).

The weight heat capacity of the process is $c=\infty$, which follows from the general relation $c=\frac{dq}{dt}$ with $t=$const. The specific work of the process is correspondingly $h=\infty$.

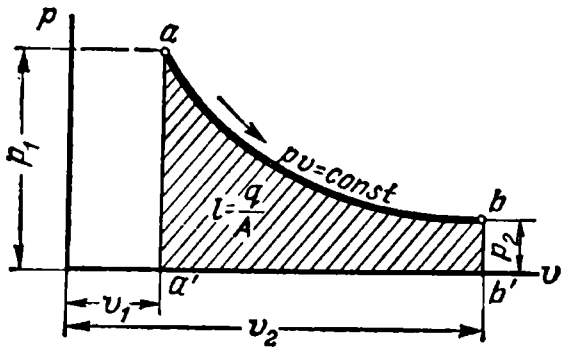


Fig. 4-3

Example 4-4. One kilogram of air expands at a constant temperature of 100° C, its volume increasing 5 times. Determine the work of expansion and the amount of heat consumed.

According to equation 4-16

$$l=RT\ln\frac{v_2}{v_1}=29.27\times373\ \ln\ 5=17{,}600\ \text{kgm/kg}$$

and according to equation 4-17

$$q=Al=\frac{17{,}600}{427}=41.15\ \text{Cal/kg}.$$

It is interesting to note that in this example it is not necessary to know the initial pressure of the air for its solution; in all cases, when $t=100°$ C, $\frac{p_1}{p_2}=\frac{v_2}{v_1}=5$, the magnitude of the work is the same; e. g., when $p_1=5$ ata and $p_2=1$ ata; $p_1=10$ ata and $p_2=2$ ata, etc.

4-5. The Adiabatic Process. The fundamental condition of the adiabatic process is the absence of an exchange of heat between the gas and the surrounding medium, i. e.,

$$dq=0. \qquad (4\text{-}18)$$

Since $dq=0$, q must also be 0, but this does not mean that every process in which $q=0$ is adiabatic. There may be processes during one part of which heat is imparted and during

another part extracted in the same quantity; for such a process as a whole $q = 0$, but it is not adiabatic because there is an exchange of heat with the surrounding medium. Therefore the essential and adequate condition for an adiabatic process is the analytical expression $dq = 0$ which means that there is absolutely no exchange of heat during the process; the condition $q = 0$ is essential to an adiabatic process, but, as we have shown, is inadequate as a definition of it.

When $dq = 0$ the equation for the first law of thermodynamics becomes

$$du + A\,dl = 0$$

whence

$$A\,dl = -du, \tag{4-19}$$

or, in detail,

$$Ap\,dv = -c_v\,dt, \tag{4-20}$$

i. e., the work of adiabatic expansion is done at the expense of the reduced internal energy of the gas, and, consequently, is connected with a reduction in its temperature; the work of adiabatic compression goes exclusively to increase the internal energy of the gas with a consequent increase in its temperature. In other words, the change in the internal energy and the work of the adiabatic process are equal in magnitude and opposite in sign.

The work of a finite process by equations 4-19 and 4-20 will be

$$l = -\int_{u_1}^{u_2} \frac{du}{A} = -\frac{1}{A}\int_{t_1}^{t_2} c_v\,dt = -\frac{1}{A}(u_2 - u_1) = \frac{1}{A}(u_1 - u_2) =$$

$$= \frac{1}{A}(c_{v_{m_1}} t_1 - c_{v_{m_2}} t_2), \tag{4-21}$$

and when $c_v = \text{const}$

$$l = \frac{c_v}{A}(t_1 - t_2). \tag{4-22}$$

As we see, the condition $dq = 0$ enabled us to determine the work l; this condition, therefore, determines the character of the curve of the process, the *adiabatic* in the system pv, i. e., the connection between the variables p and v. Let us find this connection; we know from the fundamental equation $dq = 0$ that

$$c_v\,dt + Ap\,dv = 0$$

and substituting from equation 3-30 $c_v = \frac{AR}{k-1}$

$$\frac{AR}{k-1} dt + Ap\, dv = 0,$$

or,

$$R\, dt + (k-1)\, p\, dv = 0.$$

Differentiating the characteristic equation $pv = RT$ we get

$$p\, dv + v\, dp = R\, dT,$$

so that the previous equation may be written as

$$p\, dv + v\, dp + (k-1)\, p\, dv = 0$$

whence

$$v\, dp + kp\, dv = 0.$$

Dividing this last equation by pv we get

$$\frac{dp}{p} + k\frac{dv}{v} = 0.$$

The integration of this differential equation is very simple if it be assumed that k is a constant value within the limits of the process; in which case we get

$$\ln p + k \ln v = \text{const},$$

or,

$$\ln (pv^k) = \text{const},$$

so that

$$\boxed{pv^k = \text{const},} \qquad (4\text{-}23)$$

which is the adiabatic equation in the system pv when $k = \frac{c_p}{c_v} = \text{const}$. From equation 4-23 it follows that

$$\frac{p_2}{p_1} = \left(\frac{v_1}{v_2}\right)^k, \qquad (4\text{-}24)$$

i. e., *the pressure of the gas is reduced by adiabatic expansion and increased by adiabatic compression.* For the isothermic process we had (equation 4-14)

$$\frac{p_2}{p_1} = \frac{v_1}{v_2};$$

because $k > 1$, it is obvious that in adiabatic expansion there is a greater loss of pressure than in isothermic, *i. e., the adiabatic is closer to the vertical than the isotherm in the pv system.*

The adiabatic with the equation $pv^k=\text{const}$ is an unequilateral hyperbola which does not cut the axes of its coordinates, as can be seen from equation 4-24; actually, $v_1=0$ only when $p_1=\infty$ and $p_2=0$ only when $v_2=\infty$.

When $k=\text{const}$ the equation of work may have a number of variants: substituting in equation 4-22 from equation 3-30

$$c_v=\frac{AR}{k-1},$$

we get

$$l=\frac{c_v}{A}\left(t_1-t_2\right)=\frac{R}{k-1}\left(T_1-T_2\right), \qquad (4\text{-}25)$$

and since

$$p_1v_1=RT_1, \text{ and } p_2v_2=RT_2,$$

then

$$\boxed{l=\frac{1}{k-1}\left(p_1v_1-p_2v_2\right).} \qquad (4\text{-}26)$$

This last equation may be written as

$$l=\frac{p_1v_1}{k-1}\left(1-\frac{p_2v_2}{p_1v_1}\right)=\frac{p_1v_1}{k-1}\left(1-\frac{T_2}{T_1}\right), \qquad (4\text{-}27)$$

and, substituting from equation 4-24

$$\frac{p_2}{p_1}=\left(\frac{v_1}{v_2}\right)^k$$

we get

$$\underline{l=\frac{p_1v_1}{k-1}\left[1-\left(\frac{v_1}{v_2}\right)^{k-1}\right].} \qquad (4\text{-}28)$$

Lastly, substituting

$$\frac{v_1}{v_2}=\left(\frac{p_2}{p_1}\right)^{\frac{1}{k}}$$

in equation 4-28, we get

$$l=\frac{p_1v_1}{k-1}\left[1-\left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}\right]. \qquad (4\text{-}29)$$

By comparing equations 4-27 and 4-29 we deduce

$$\boxed{\frac{T_2}{T_1}=\left(\frac{v_1}{v_2}\right)^{k-1}=\left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}} \qquad (4\text{-}30)$$

and, consequently,

$$Tv^{k-1} = \text{const}$$

and

$$Tp^{\frac{1-k}{k}} = \text{const}.$$

The first equation is that of the adiabatic when k=const in the system Tv and the second in the system Tp.

When k is a variable the relations between p, v and T are much more complicated, even assuming the straight-line dependence of k on temperature, and for practical calculations they are inconvenient. In analytical calculations, therefore, the equation we have evolved is normally applied, k being taken as a constant and its dependence on the temperature accounted for by using the average value of k for the process when t_1 and t_2 are known, or by an approximation if only one of the temperatures is known.

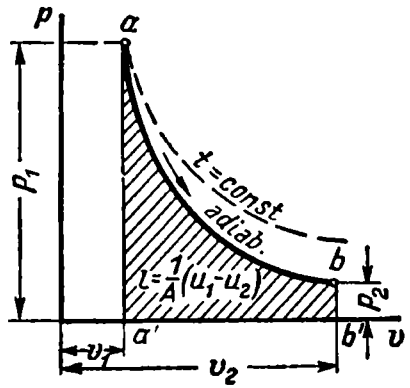


Fig. 4-4

Fig. 4-4 is the graphic representation in the system pv of an adiabatic expansion of a gas; as we have said, the adiabatic is closer to the vertical than the isotherm. Area $abb'a'$ below the adiabatic curve ab gives, in the present case, the work l as well as the change in the internal energy of the gas

$$\frac{1}{A}(u_1 - u_2).$$

The weight heat capacity of the process is c=0 which follows from the general relation $c = \frac{dq}{dt}$ when dq=0. Since $c=c_v+h$ in the general case, the specific work of the adiabatic process is $h=-c_v$.

Example 4-5. One kilogram of air at a temperature of 30° C and an initial pressure of 1 ata is compressed adiabatically to 10 ata. Determine the work of compression.

Assuming, to begin with, that k=1.4 we get from equation 4-30

$$T_2 = T_1\left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}} = 303 \times 10^{\frac{0.4}{1.4}} = 585° \text{ K};$$

$$t_2 = 585 - 273 = 312° \text{ C}.$$

For the average temperature

$$t_m = \frac{t_1 + t_2}{2} = \frac{30 + 312}{2} = 171^\circ \text{C};$$

according to equation 3-30

$$k = 1.4 - (0.00005 \times 171) = 1.39.$$

Using this value we get

$$T_2 = 303 \times 10^{\frac{0.39}{1.39}} = 577^\circ \text{K}$$

and

$$t_2 = 577 - 273 = 304^\circ \text{C}.$$

In which case, according to equation 4-25

$$l = \frac{R}{k-1}(t_1 - t_2) = \frac{29.27}{0.39}(30 - 304) = -20{,}600 \text{ kgm/kg}$$

(the minus sign shows that the work is that of compression).

Example 4-6. To what pressure must air be adiabatically compressed to raise its temperature to 600° C if its initial pressure is 1 ata and initial temperature 100° C, and what is the work of compression?

From the tables in the appendices we find that $c_{p_{m_1}} = 0.24$ and $c_{p_{m_2}} = 0.251$; since AR for air $= \frac{29.27}{427} = 0.068$, then $c_{v_{m_1}} = c_{p_{m_1}} - AR = 0.24 - 0.068 = 0.172$, and $c_{v_{m_2}} = 0.251 - 0.068 = 0.183$.

In this case the work, by equation 4-21,

$$l = 427[(0.172 \times 100) - (0.183 \times 600)] = -39{,}600 \text{ kgm/kg}.$$

For the average temperature

$$t_m = \frac{100 + 600}{2} = 350^\circ \text{C};$$

applying equation 3-30,

$$k = 1.4 - 0.00005 \times 350 = 1.383$$

and applying equation 4-30 we get

$$p_2 = p_1 \left(\frac{T_2}{T_1}\right)^{\frac{k}{k-1}} = \left(\frac{873}{373}\right)^{\frac{1.383}{0.383}} = 21.38 \text{ ata}.$$

Example 4-7. Air with an initial pressure of 0.9 ata and a temperature of 45° C is compressed adiabatically to one-fifth of its original volume. Determine the pressure and temperature at the end of the compression.

If we assume $k = \frac{c_p}{c_v}$ to be a constant value and equal to 1.4, then by applying equation 4-24 we get

$$p_2 = p_1 \left(\frac{v_1}{v_2}\right) = 0.9 \times 5^{1.4} = 8.6 \text{ ata},$$

and from equation 4-30 we get

$$T_2 = T_1 \left(\frac{v_1}{v_2}\right)^{k-1} = (273+45)\times 5^{0.4} = 608^\circ \text{ K}$$

and

$$t_2 = 608 - 273 = 335^\circ \text{ C}.$$

4-6. The Polytropic Process. The equation of the *polytropic process* in the system pv, as we have already stated, is

$$\boxed{pv^n = \text{const}} \tag{4-31}$$

where the exponent n is also, for the given process, a constant and may have any numerical value. The processes we have analysed—isochoric, isobaric, isothermic and adiabatic—are particular cases of the polytropic process and each of them has a corresponding value for n=const. It is not difficult to see that

for the isochoric process $n = \pm\infty$;
for the isobaric process $n = 0$;
for the isothermic process $n = 1$;
for the adiabatic process $n = k = \frac{c_p}{c_v} = \text{const}$.

Actually, when $n=0$ equation 4-31 gives us p=const; when $n=1$ the equation of the isotherm is pv=const and when $n=k$ the equation of the adiabatic is pv^k=const (when $k=\frac{c_p}{c_v}$=const).

If, from equation 4-31, we extract the root to the nth power we shall get, for the general case, the equation of the polytrope in the form $p^{\frac{1}{n}} \times v$=const, which, when $n=\pm\infty$ gives v=const.

From equation 4-31 it follows that

$$\frac{p_2}{p_1} = \left(\frac{v_1}{v_2}\right)^n. \tag{4-32}$$

Since the polytrope equation pv^n=const and the adiabatic equation pv^k=const are identical in form and differ only in the constant exponent of v it follows that all the variations of the equation of work that we obtained for the adiabatic pv^k=const may be applied to the polytropic process by exchanging the values k and n. Thus, we may write, employ-

ing all the equations from 4-25 to 4-29

$$l=\frac{R}{n-1}(T_1-T_2)=\frac{1}{n-1}(p_1v_1-p_2v_2)=\frac{p_1v_1}{n-1}\left(1-\frac{T_2}{T_1}\right)=$$

$$=\frac{p_1v_1}{n-1}\left[1-\left(\frac{v_1}{v_2}\right)^{n-1}\right]=\frac{p_1v_1}{n-1}\left[1-\left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}\right] \quad (4\text{-}33)$$

and by analogy with equation 4-30

$$\frac{T_2}{T_1}=\left(\frac{v_1}{v_2}\right)^{n-1}=\left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}. \quad (4\text{-}34)$$

Let us determine the magnitude of the specific work of the process $h=\frac{A\,dl}{dT}$, for which we shall employ the expression for the work l from equation 4-33

$$l=\frac{R}{n-1}(T_1-T_2)=\frac{R}{1-n}(T_2-T_1);$$

for an infinitely small change of state it is obvious that $dl=\frac{R}{1-n}dT$ and, consequently,

$$h=\frac{A\,dl}{dT}=\frac{AR}{1-n}=\text{const}, \quad (4\text{-}35)$$

that is, *the polytropic process is one in which the specific work is a constant.*

The weight heat capacity of the process (equation 3-8)

$$c=c_v+h=c_v+\frac{AR}{1-n}=\frac{c_v-nc_v+AR}{1-n}=$$

$$=\frac{c_p-nc_v}{1-n}=c_v\frac{k-n}{1-n}. \quad (4\text{-}36)$$

From equation 4-36 we obtain in particular cases:
for the isochoric process, i. e., $n=\pm\infty$, $c=c_v$;
for the isobaric process, i. e., $n=0$, $c=kc_v=c_p$;
for the isothermic process, i. e., $n=1$, $c=\infty$;
for the adiabatic process, i. e., $n=k$, $c=0$
which agrees with conclusions drawn above. From the same equation we see that the heat capacity c may be negative, since $c<0$ when $k>n>1$; in other words, c is negative for polytropes that lie between an isotherm and an adiabatic passing through a given point.

Since $c=\frac{dq}{dt}$, negative heat capacity means that dq and dt have opposite signs. Despite the fact that heat is imparted to the gas its temperature drops; an increase in temperature

takes place when heat is taken from the gas. Although, at first glance, both these statements are somewhat unusual, they can easily be explained with the aid of the fundamental equation

$$q = u_2 - u_1 + Al,$$

because precisely in such processes $Al > q$ (in its absolute magnitude).

Therefore, in performing the work, l, in addition to the heat, q, imparted to the gas, part of its internal energy is

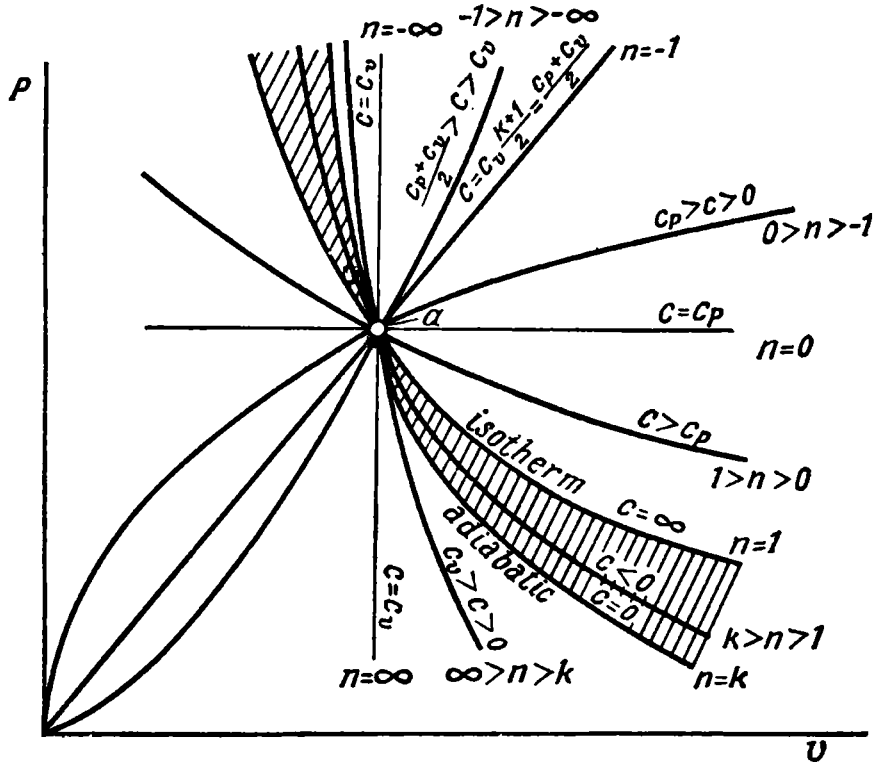


Fig. 4-5

consumed, so that as a result of the process of expansion $u_2 < u_1$ and, consequently, $t_2 < t_1$. In cases of compression the work l is transformed into its heat equivalent Al, and since the amount of heat $q < Al$ is taken from the gas, the surplus heat $(Al - q)$ remains in the gas and is used to increase its internal energy, and, consequently, its temperature.

Fig. 4-5 contains a group of polytropes in the system pv passing through a given point a, each polytrope being

for a different value of the constant exponent n. The diagram shows the relative positions of the polytropes and the difference in their characters. When $\infty > n > 0$, the polytrope is a hyperbola—such, in particular, are the isotherm and the adiabatic; when $0 > n > -\infty$, the polytropes are curves that pass through the point of origin of the coordinate system—when $n > -1$, the curve is convex and when $n < -1$ it is concave; when $n = -1$, however, the polytrope is a straight line. The heat capacity c is negative for the polytropes passing through point a in the shaded area.

A polytrope in the system pv approaches more closely to the vertical, the greater the absolute value of the constant exponent n, this exponent being inversely proportional to the length of the subtangent of the polytrope. Applying the laws of analytical geometry to the present case, the value of the subtangent of any curve in the system pv is $m = p\frac{dv}{dp}$.

Differentiating the polytrope equation, $pv^n = \text{const}$ we get $pnv^{n-1}dv + v^n dp = 0$

whence

$$m = p\frac{dv}{dp} = -\frac{v}{n},$$

i. e., the length of the subtangent of a polytrope in the system pv is equal to the abscissa of a point divided by the exponent of the given polytrope. From this it follows that the greater the absolute value of the exponent n, the shorter the subtangent and the closer the polytrope to the vertical. In particular, the adiabatic is more vertical than the isotherm because $k > 1$; the flattest of the polytropes is the isobar, a horizontal straight line, for which $n = 0$; the isochor is the steepest, being a vertical straight line for which $n = \pm\infty$.

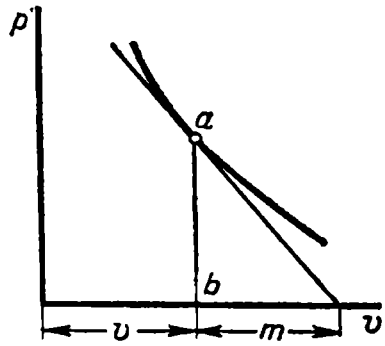


Fig. 4-6

Thus we have a simple means of using the pv diagram to determine graphically the exponent n of the polytrope (Fig. 4-6). To do this we draw the tangent to the polytrope

at any given point a, and find the length of the subtangent m. The quotient $(-\frac{v}{m})$ gives the value of the exponent n. The subtangent m will be positive if it lies to the left of point b on the axis of the abscissa and negative if it lies to the right.

In Sec. 4-5 we found that the specific work is $h=-c_v$ for an adiabatic process. And since the heat capacity c_v is a variable for real gases, the specific work h will also be a variable, i. e., the adiabatic process is not really polytropic and cannot, therefore, be expressed by an equation of the pv^n -const type (as we have pointed out above). It is only when we assume that c_v is a constant, and that $k=\frac{c_p}{c_v}$ is also a constant, that we get a simplification of the adiabatic equation, i. e., pv^k—const, and the adiabatic becomes a polytrope.

Since $dq=c\ dt$, for the general case

$$q=\int_{t_1}^{t_2} c\,dt=\int_{t_1}^{t_2} c_v\frac{k-n}{1-n}\,dt,$$

where c_v and k depend on the temperature. When c_v, and, consequently, k are constant

$$q=c(t_2-t_1)=c_v\frac{k-n}{1-n}(t_2-t_1).$$

Now let us determine, for the process under discussion, the value of $\frac{du}{A\,dl}$; applying equations 4-35 and 3-31, we get

$$\frac{du}{A\,dl}=\frac{c_v\,dt}{h\,dt}=\frac{c_v}{h}=\frac{AR}{k-1}\times\frac{1-n}{AR}=\frac{1-n}{k-1};$$

when k=const this is a constant magnitude. It therefore follows that in a polytropic process where k=const, the parts of the total heat q expended in increasing the internal energy (u_2-u_1) and on the work of expansion Al have a constant interrelation that is determined for the given gas by the polytrope exponent n. In particular, for the isobaric process, $(n=0)\frac{du}{A\,dl}=\frac{1}{k-1}$.

If any polytrope in the pv diagram is given, its exponent n is determined simply and analytically by the coordinates of any two of its points p_1, v_1 and p_2, v_2, since

$$p_1v_1^n=p_2v_2^n.$$

Expressing this equation logarithmically, we get

$$\log p_1 + n \log v_1 = \log p_2 + n \log v_2$$

whence

$$n = \frac{\log p_2 - \log p_1}{\log v_1 - \log v_2}$$

and, furthermore, the values of p_1, p_2, v_1 and v_2 may be taken directly from the diagram in millimetres, irrespective of the scale of the coordinates.

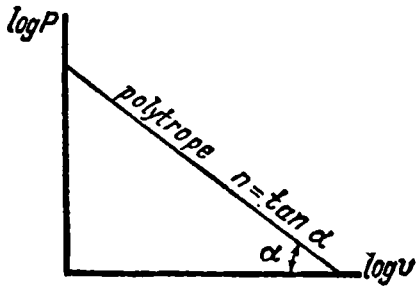


Fig. 4-7

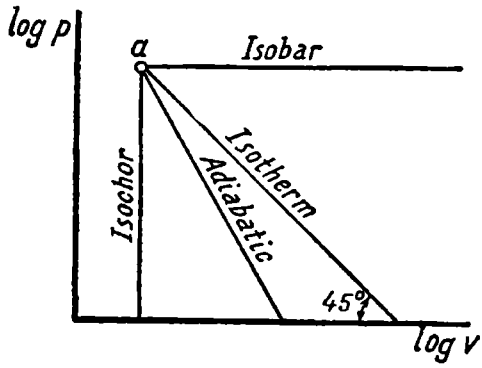


Fig. 4-8

Polytropic processes may be represented by very simple graphs with logarithmic coordinates (log p and log v); if we express the polytrope equation,

$$pv^n = \text{const}$$

by logarithms we get

$$\log p + n \log v = \text{const}.$$

This is a straight-line equation with the angle coefficient $n = \tan \alpha$ (Fig. 4-7). Therefore, all polytropes when expressed logarithmically produce straight-line graphs; the angle α determines the polytrope exponent n and vice versa. Fig. 4-8 is a logarithmic graph showing an isobar ($\alpha = 0°$), an isochor ($\alpha = 90°$), an isotherm ($\alpha = 45°$) and an adiabatic (α is greater than 45°), all passing through point a.

Chapter Five

THE SECOND LAW OF THERMODYNAMICS

5-1. The Cycle, or Cyclic Process. In any heat engine, that is, an engine in which heat is transformed into work, the working body (gas or steam) undergoes a process of expansion, because positive work can only be performed by expansion. The continued uninterrupted action of the engine and, therefore, the possibility of obtaining the large quantities of work required, involves the constant repetition of the process of expansion by the working body. Such repetition is obtained in two ways: 1—the working body is removed from the engine once the work of expansion has been completed and a further portion is introduced in the same quantity and in the same initial state to start the process of expansion over again; 2— the working body, having completed the process of expansion, returns to its initial state and repeats the process. Obviously in the second case the engine works continuously with the same portion of gas or steam, which is desirable theoretically and, occasionally, practically. After expansion it is possible for the body to return to its initial state only by compression, to effect which work by an outside agency must be expended; the process of compression chosen must necessarily require less work than that obtained by expansion, i. e., the curve of compression *cda* must lie below the curve of expansion *abc* in the system *pv* (Fig. 5-1). The working body of the engine, therefore, changes its state in accordance with the enclosed figure *abcda*, alternately expanding and compressing and periodically returning to its initial state *a*. This process is called a *cycle*, or *cyclic process*. Along the line *abc* the body performs the work of expansion l_1=area *abcc'a'*, and along the line *cda* its compression involves the work l_2=area *adcc'a'* (l_2 is the absolute magnitude of the work of compression); since the work of expansion is positive

and the work of compression negative, the body, as the result of one cycle, performs the positive work $l=l_1-l_2$, which is measured as the difference in the two areas, i. e., the area of the closed figure of the cycle *abcda*.

The work of the cycle, therefore, is graphically depicted in the system *pv* as the area of a closed figure, and it is obviously positive if the process is in a clockwise direction as in Fig. 5-1 and negative if counterclockwise. The first direction of the process ($l>0$) is typical of heat engines of various

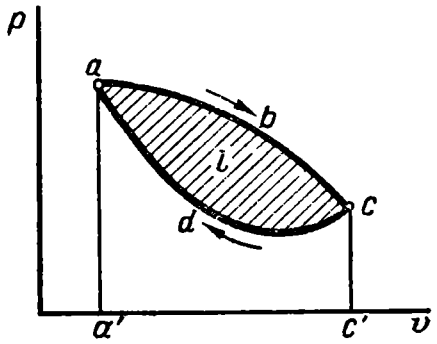


Fig. 5-1

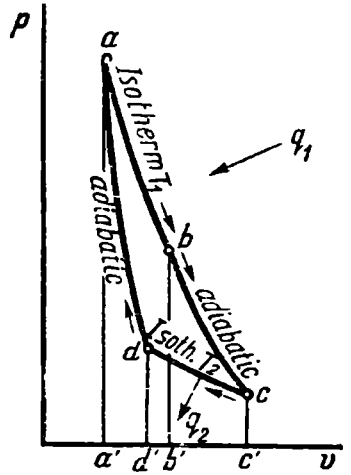


Fig. 5-2

types since they are machines developing mechanical energy (the direct process); the opposite direction ($l<0$) indicates the expenditure of mechanical energy on a machine that is driven by an outside agency, such as refrigerating machinery and the so-called heat pumps (reverse process).

Like every other process the cycle may be reversible and irreversible; the basic conditions of reversibility are, as we know, mechanical and thermal equilibrium and the absence of friction.

5-2. The Carnot Cycle for an Ideal Gas. We shall now examine the simplest cyclic process proposed by the French engineer Carnot in 1824 as that of an ideal heat engine; it consists of two isotherms and two adiabatics. This type of reversible process is depicted in the *pv* system for 1 kg of gas (Fig. 5-2). The gas, whose initial state is point *a* (regarded as ideal), expands, first according to isotherm *ab* during which its volume increases from v_a to v_b and performs

work equal to area $abb'a'$, equivalent to an amount of heat q_1 imparted from outside sources with a constant temperature of T_1. By equation 4-17, this amount of heat is expressed as

$$q_1 = ART_1 \ln \frac{v_b}{v_a}. \qquad (5\text{-}1)$$

At point b the transfer of heat to the gas stops, and it continues to expand to volume v_c, along adiabatic bc, performing work equal to area $bcc'b'$, exclusively by virtue of its internal energy, as a result of which its temperature falls from T_1 at point b to T_2 at point c. Beginning from point c, the gas returns to its original state at point a in two stages; at first it is compressed along isotherm cd when its volume decreases from v_c to v_d, and the work of an outside agency is expended equal to area $dcc'd'$ and an equivalent amount of heat q_2 is taken from the gas and imparted to an outside *cooling medium* with a constant temperature of T_2. By equation 4-17 the absolute magnitude of this amount of heat is

$$q_2 = ART_2 \ln \frac{v_c}{v_d}. \qquad (5\text{-}2)$$

The extraction of heat ceases at point d which is selected so that the gas, continuing to compress adiabatically, will return to its original state at point a. The outside agency expends on this final adiabatic compression, da, an amount of work equal to area $add'a'$ exclusively on increasing the internal energy of the gas so that its temperature rises from T_2 to T_1.

Thus, as a result of the full cycle the gas receives at stage ab the amount of heat q_1 from an outside agency, at stage cd it transfers the amount of heat q_2 to the outside agency and performs the work l, measured in mechanical units, as represented by the area $abcd$.

Since, in a full cycle, the final state coincides with the initial state (point a), in equation 2-7 of the first law of thermodynamics

$$q = u_2 - u_1 + Al$$

the values of the internal energy are $u_2 = u_1 = u_a$ as a result of which the equation becomes very simple:

$$q = q_1 - q_2 = Al, \qquad (5\text{-}3)$$

i. e., the amount of heat q is equal to the difference in the amounts of heat imparted to and taken from the working body and is the equivalent of the work of the cycle, l.

Substituting in equation 5-3 the values of q_1 and q_2 from equations 5-1 and 5-2, we get

$$Al = q = q_1 - q_2 = AR\left(T_1 \ln \frac{v_b}{v_a} - T_2 \ln \frac{v_c}{v_d}\right). \qquad (5\text{-}4)$$

But for the adiabatic *bc*, according to equation 4-30,

$$\frac{T_2}{T_1} = \left(\frac{v_b}{v_c}\right)^{k-1}$$

and similarly for the adiabatic *ad*

$$\frac{T_2}{T_1} = \left(\frac{v_a}{v_d}\right)^{k-1}.$$

Consequently,

$$\frac{v_b}{v_c} = \frac{v_a}{v_d} \text{ or } \frac{v_b}{v_c} = \frac{v_c}{v_d}. \qquad (5\text{-}5)$$

The relation of the greater volume to the smaller in any change of state is called the *compression ratio* or *expansion ratio* depending on the change. According to equation 5-5, *in the cycle under discussion, the isothermic ratios of expansion and compression are identical.* To express them we introduce

$$\delta = \frac{v_b}{v_a} = \frac{v_c}{v_d}$$

and obtain, after the corresponding substitution in equation 5-4

$$Al = AR\,(T_1 - T_2) \ln \delta. \qquad (5\text{-}6)$$

This is the work we have obtained as the difference between the quantities of heat q_1 and q_2, but for the isothermic processes *ab* and *dc*

$$q_1 = Al_{ab} \text{ and } q_2 = Al_{dc};$$

therefore,

$$l = l_{ab} - l_{dc},$$

i. e., the work of the Carnot cycle is equal to the difference in the work of the isothermic processes; from this we may conclude that the work of the adiabatic processes has the same absolute magnitude in both directions. By equation 4-21

$$l_{bc} = \frac{1}{A}(u_b - u_c) \text{ and } l_{da} = \frac{1}{A}(u_d - u_a)$$

but $u = u_a$ and $u_d = u_c$; therefore,

$$l_{bc} = -l_{da},$$

so that the work expended on adiabatic compression is replaced during adiabatic expansion.

Summarising all that has been said above, we come to the conclusion that in order to effect the cyclic process described and in so doing convert heat into work, there must be (1) a source of heat with a constant temperature of T_1 from which each kilogram of gas acquires q_1 of heat for the cycle; (2) a cooling medium with a constant temperature of $T_2 < T_1$ which extracts from each kilogram of the gas an amount of heat $q_2 < q_1$; and (3) a working body, a gas that retains the amount of heat $q = q_1 - q_2$ and converts it into work l, so that, according to the first law of thermodynamics, $q = Al$. The work l of the cycle, therefore, is obtained by expending heat from the source to the amount of q_1. It is typical that not all the heat q_1 obtained from the source is converted into work, but only a part, q, of it; the remainder of the heat, $q_2 = q_1 - q$, is given up by the gas to the cooling medium and, therefore, is not used in this process and for the cycle may be regarded as waste heat. The work obtained is, therefore, connected with the transfer of the amount of heat q_2 from the source of heat to the cooling medium, i. e., from a body with a higher temperature to one with a lower temperature, through the agency of the working body, the gas. The amount of heat q_2 which is transferred to the cooling medium, is, to a certain extent, of no practical value in the given cycle since it is waste heat; although retained quantitatively, it changed qualitatively by its transition from a body with a higher temperature T_1 to a body with a lower temperature T_2. To use this heat, not only by converting it into work, but even for simple heating purposes, a body of even lower temperature than T_2 would be needed, which in practice is not always available. The waste heat q_2 is less, the lower the temperature of the cooling medium T_2, as can be seen from equation 5-2; q_2 would be equal to zero only in the impossible case of a cooling medium maintained at a temperature of absolute zero, i. e., —273° C.

Thus, the practical implementation of a Carnot cycle in which the heat from the source q_1 would be converted into work in its entirety is impossible; part of the heat q_1 from the source is transferred to the cooling medium and is not

converted into work, so that to obtain the work l it is necessary to expend an amount of heat from the source $q_1 = Al + q_2$, the heat expended, q_1, being greater than Al.

The employment of heat in a cyclic process whose purpose is to obtain work is assessed as the *thermal efficiency of the cycle*

$$\boxed{\eta_t = \frac{Al}{q_1}}, \tag{5-7}$$

which is, *therefore, the relation of the work of the process to the amount of heat obtained from a source and expended on that work*. Using equation 5-3 we may express the thermal efficiency in a number of ways:

$$\eta_t = \frac{Al}{q_1} = \frac{q}{q_1} = \frac{q_1 - q_2}{q_1} = 1 - \frac{q_2}{q_1}. \tag{5-8}$$

It is obvious that η_t will always be less than 1; an important task for thermodynamic research is to study methods of increasing η_t, that is, of making the cycle of heat engines more economical.

The efficiency of the Carnot cycle we have studied is (applying equation 5-7 and connecting it with equations 5-1 and 5-6)

$$\eta_t = \frac{Al}{q_1} = \frac{AR(T_1 - T_2)\ln\delta}{ART_1 \ln\delta} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}. \tag{5-9}$$

Thus, the efficiency of the Carnot reversible gas cycle is fully determined by the relation of the temperatures, T_1 and T_2, of the cycle; it is the greater the more T_1 increases and T_2 diminishes and, therefore, is greater as the difference between them, *i. e., the drop in temperature during the cycle or the temperature degradation*, increases. The loss of temperature in the cycle is an absolute condition for the performance of work, because when $T_2 = T_1$ the efficiency, $\eta_t = 0$, that is, there is no work. In practice η_t is always less than 1, i. e., not all the heat transferred from the source and used in the cycle is converted into work; it is only in the abstract case that $\eta_t = 1$, that is when $T_2 = 0$, in which case the cooling medium would have to be maintained at a temperature of absolute zero.*

* According to Nernst's heat theorem it is impossible to reach absolute zero ($T = 0°$ K) either practically or theoretically. Therefore, with a finite difference in temperature between the source of heat and the cooling agent η_t is always less than unity.—*Ed.*

We shall now obtain confirmation of the fact that it is impossible to reach a temperature lower than absolute zero, or —273° C; if it were possible to obtain a lower temperature, that is, if T_2 were less than 0, the efficiency of the Carnot cycle would be greater than 1, and $Al > q_1$, which contravenes the first law of thermodynamics and the principle of the conservation of energy.

Methods of increasing the efficiency of the Carnot cycle are increasing the temperature T_1 of the source of heat and decreasing the temperature T_2 of the cooling medium; the cooling media most easily available and most used in practice in heat engines are atmospheric air and water, the average temperature of which may be assumed as equal to 10° C. When $T_2 = 273 + 10 = 283°$ K, increases in T_1 produce the following results:

$t_1 = 200$	400	600	800	1,000	1,200°C.
$T_1 = 473$	673	873	1,073	1,273	1,473°K
$\eta_t = 0.4$	0.58	0.68	0.74	0.78	0.81.

The efficiency of the Carnot reversible cycle is $\eta_t = 1 - \frac{T_2}{T_1}$ where T_1 is the temperature of the source of heat and T_2 temperature of the cooling medium, which we obtained for ideal gases with the characteristic equation $pv = RT$ when $k = \frac{c_p}{c_v} = \text{const}$. Since the gas constant R does not enter into the expression for efficiency, it is obviously identical for all ideal gases. A specific feature of the Carnot cycle is that its efficiency does not in any way depend on the nature of the working body, as we shall see somewhat later (Sec. 5-5), i. e., for given T_1 and T_2 it is identical, not only for all real gases, but also for the vapours of all fluids, and is greater than the efficiency of any other cycle within the same temperature limits. The Carnot cycle, therefore, is the ideal theoretical cycle for any heat engine although it cannot be realised in practice for a number of reasons.

It must not be forgotten that the efficiency we obtained for the Carnot cycle is that of a reversible cyclic process; all real processes, as we know, are irreversible, their irreversibility being due to loss of work. Therefore, the efficiency of the Carnot cycle is always less than the theoretical $\eta_t = 1 - \frac{T_2}{T_1}$ where T_1 and T_2 are the absolute temperatures of the source of heat and the cooling medium. If, for example, the condi-

tions of thermal equilibrium are not fulfilled and the gas expands isothermically at a temperature T_1' that is less than T_1 and is compressed at a temperature of T_2' that is greater than T_2, it is obvious that the efficiency of the cycle, $\eta_t' = 1 - \frac{T_2'}{T_1'}$ will be less than $1 - \frac{T_2}{T_1}$. The turbulence due to the absence of mechanical equilibrium and the presence of friction both cause loss of work, i. e., reduce the efficiency of the cycle.

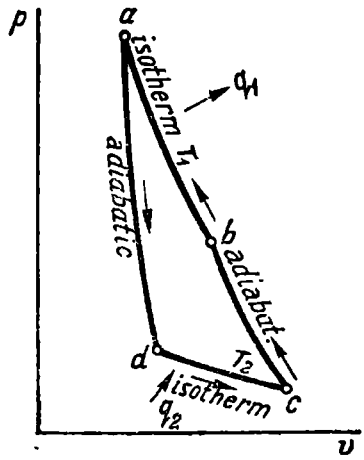


Fig. 5-3

5-3. The Carnot Reverse Cycle. We shall now examine Carnot's reverse cycle, the process depicted in the *pv* graph in a counterclockwise direction (Fig. 5-3). Gas in its initial state at point *a* first expands adiabatically along curve *ad* with the temperature falling from T_1 to T_2, and then proceeds according to isotherm *dc*. During its isothermic expansion the gas receives a quantity of heat q_2 from an external body with a constant temperature of T_2.

Further the gas is compressed, at first adiabatically as *cb*, after which the temperature rises from T_2 to T_1 and compression then continues along isotherm *ba*. In the case of isothermic compression the gas transfers the quantity of heat q_1 to an external body with a constant temperature of T_1. External work l is expended on the complete cycle *adcb*; it is measured in the usual way by area *abcd* and is converted into the equivalent amount of heat $q = Al$; from the cold body with a temperature of T_2 the amount of heat q_2 is obtained and the warm body with a temperature of T_1 has the quantity of heat q_1 imparted to it.

But according to the equation of the first law, for the given cycle

$$q_2 - q_1 = -Al$$

where q_1 and l are absolute magnitudes, i. e.,

$$q_1 = q_2 + Al.$$

Thus, as a result of the *adcb* cycle, a quantity of heat q_2 is transferred from a cold body to a warm body through the medium of the gas by means of externally expended work; in other words, the amount of heat q_2 is raised from a low temperature level to a higher level, so that an installation working according to this cycle may be termed a *heat pump*. As we have seen, work applied externally is a necessary condition for the transfer of heat from a cold body to a warm body; such a transfer is impossible without the expenditure of work.

Carnot's reverse cycle is the ideal cycle for *refrigerating installations*. At the given temperature t_1 (the temperature of the room, for example, say 20° C) it is possible, by selecting the correct degree of adiabatic expansion, to obtain a low temperature t_2 in the refrigerator installation (say, −10° C). In the case of the isothermic expansion *dc*, the gas, when at this temperature, absorbs the amount of heat q_2 from the premises being cooled and thus retains it theoretically at this temperature, but practically at a temperature that is slightly higher.

5-4. The Second Law of Thermodynamics. The first law of thermodynamics establishes the equivalence of heat and mechanical energy and the quantitative relation that obtains when one form of energy is converted into another; it says nothing about the conditions under which the transformation is possible. The conversion of work into heat is, in general, not connected with any difficulties and limitations; for example, the work of friction, the work of compression, the work expended on the Carnot reverse cycle are all transformed fully into heat; the work of any engine can be transformed wholly into heat by braking the engine. The conversion of heat into work is a different matter. In the Carnot cycle, which, as we have said, is the ideal and most economical cycle, the heat cannot be fully transformed into work; part of the heat is not employed in the cycle and is a kind of waste, it is transferred from a higher temperature level to a lower and is, to a certain extent, valueless, its quality being lowered. Further, we saw that for the Carnot cycle to make use of the heat provided by the source, a cooling medium is necessary, i. e., a body at a temperature lower than that of the source—a drop in temperature is essential.

The impossibility of converting the entire heat of the source into work and the necessity of there being a cooling medium, a body whose temperature is lower than that of the source, to which part of the heat supplied by the source is inevitably transferred without being transformed into work, are not, of course, peculiarities of the Carnot cycle but are features of every cyclical process because, as will be demonstrated below, any cycle can be broken up into a number of elementary Carnot cycles, the sum of which will give results identical with those of the given cycle.

The absence of bodies with a natural temperature that is lower than that of atmospheric air or the waters of the seas and rivers means that the tremendous reserves of free heat energy contained in them cannot be used in practice for conversion into work; the artificial lowering of temperature, as we have seen, involves the expenditure of an amount of work which is equal to the work of an engine having the same drop in temperature.

All natural heat processes are one-sided and consist either in the transfer of heat from a body at a high temperature to one with a lower temperature, by which temperatures are equalised, or in the conversion of work into heat. The reverse transfer of heat from a cold to a warm body is impossible without outside help, given our conceptions of terrestrial conditions; as we have seen, work must be performed to raise heat from a lower temperature level to a higher.

The conversion of heat into work is only possible if certain special conditions are observed.

The specific nature of heat energy, understood as the energy of infinitely small particles of a body, is due to its being the energy of irregular, chaotic motion. Such motion is the *most probable*. Any regulated motion is easily disturbed, i. e., it shows a tendency to become irregular, irregularity being the more probable state. Since the chaotic heat motion of particles is the most probable, all other forms of energy are easily converted into heat. The reverse transition is a transition from a more probable to a less probable state which, generally speaking, is difficult and is only possible when certain conditions exist.

All artificial processes are always accompanied by an additional natural process. The conversion of heat into work, for example, is always accompanied by the transfer of heat from a source to a cooling agent; the transfer of heat from a

colder to a warmer body is connected with the conversion of the work expended on the cycle into heat.

These properties possessed by heat energy constitute the basis of *the second law of thermodynamics*; the law is formulated differently by different authors, the most widespread being the following.

1. Heat cannot flow spontaneously from a cold to a warm body, there must be an expenditure of work.

2. For heat to be converted into work there must be, in addition to the source of heat, a cooling agent possessing a lower temperature, i. e., there must be a drop in temperature.

3. The heat of the cooler body in the given system cannot serve as a source of work.

4. In a cyclic process the heat from the source cannot be converted into work in its entirety.

5. All natural processes are a transition from a less probable to a more probable state.

All these formulations are indicative of one and the same property of heat energy although they approach it from different angles.

5-5. The Carnot Theorem. By applying the second law of thermodynamics we can offer proof of the *Carnot theorem* which states that the efficiency of the Carnot reversible cycle does not depend on the nature of the working body. Let us suppose that two engines, A and B (Fig. 5-4), are working

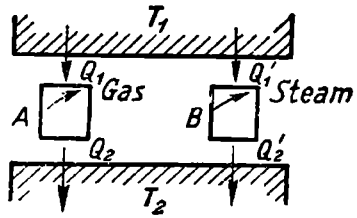


Fig. 5-4

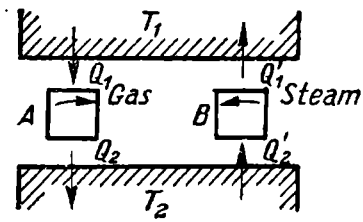


Fig. 5-5

according to the Carnot reversible cycle between the same temperature limits T_1 and T_2, the former being the constant temperature of the source of heat and the latter that of the cooling agent, and are doing identical work L; the working body of engine A is gas and that of engine B any steam. The gas receives the amount of heat Q_1 from the source and transfers the amount Q_2 to the cooling agent; the steam acquires

the amount of heat Q_1' and transfers Q_2', while $AL = Q_1 - Q_2 = Q_1' - Q_2'$. Thus the efficiencies of the gas engine η_t and of the steam engine η_t' are

$$\eta_t = \frac{AL}{Q_1} \text{ and } \eta_t' = \frac{AL}{Q_1'} \text{ respectively.}$$

Let us examine the three cases:

1) $\eta_t' > \eta_t$, i. e., $Q_1' < Q_1$;
2) $\eta_t' < \eta_t$, i. e., $Q_1' > Q_1$;
3) $\eta_t' = \eta_t$, i. e., $Q_1' = Q_1$.

Let us assume the first case to be true and make machine A complete a reverse cycle on which the amount of work L will be expended; we shall use the steam engine B (Fig. 5-5) to drive the machine A. It goes without saying that the transfer of machine A to the reverse cycle does not mean a change in the direction of the rotation of its main shaft; a marine engine works in both directions, forward and reverse, while performing the direct cycle; the arrows on Figs. 5-4 and 5-5 show the direction of the cycle effected in the machine and not the direction of rotation. The work of the system described, that of the steam engine B, driving the gas heat pump, A, proceeds as follows. The steam, as previously described, obtains the amount of heat Q_1' from the source and gives up the amount Q_2' to the cooling agent while doing the amount of work $AL = Q_1' - Q_2'$, the gas obtains the amount of heat Q_2 from the cooling agent and transfers to the source of heat the amount $Q_1 = Q_2 + AL$. And so we have the equations familiar to us

$$Q_1' - Q_2' = Q_1 - Q_2 = AL$$

and

$$Q_1 - Q_1' = Q_2 - Q_2',$$

that is, as the result of one cycle of the whole system, the source of heat acquires $Q_1 - Q_1'$ Cal, Q_1 being greater than Q_1', and gives up the same amount to the cooling agent, so that in the final analysis the work of the system is equal to zero, because the work of the engine B is consumed by the pump A. In the given system, therefore, we have a transfer of the quantity of heat $Q_2 - Q_2' = Q_1 - Q_1'$ from the cold body to the warm body without the expenditure of work, which is contrary to the second law of thermodynamics. From this

we may conclude that the first case is not true and that η_t' cannot be greater than η_t.

Let us now assume the second case to be true and make B a machine performing a reverse cycle and use A as a gas engine to drive it (Fig. 5-6). We still have the same equation

$$Q_1 - Q_2 = Q_1' - Q_2' = AL$$

and, consequently,

$$Q_1' - Q_1 = Q_2' - Q_2,$$

i.e., the source obtains the amount of heat $Q_1' - Q_1$ Cal ($Q_1' > Q_1$) and the same amount is given up by the cooling agent, so that this amount of heat is transmitted from the colder to the hotter body without an expenditure of work, which is impossible.

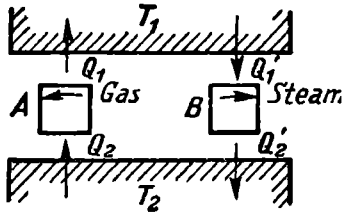


Fig. 5-6

Since, therefore, η_t' cannot be greater or smaller than η_t they obviously must be equal. For all gases $\eta_t = 1 - \frac{T_2}{T_1}$ and from the above it follows that for all steams the efficiency of the Carnot cycle may be expressed by the same equation, that is, by the temperature limits of the process; in other words, efficiency does not depend on the nature of the working body.

5-6. The Entropy of a Body. In the Carnot reversible cycle

$$\eta_t = 1 - \frac{q_2}{q_1} = 1 - \frac{T_2}{T_1}$$

where q_1 = the amount of heat received by the working body from the source of heat whose temperature is T_1;

q_2 = the absolute magnitude of the amount of heat transferred by the body to the cooling agent whose temperature is T_2.

Therefore,

$$\frac{q_2}{q_1} = \frac{T_2}{T_1}$$

and

$$\frac{q_1}{T_1} = \frac{q_2}{T_2}.$$

Since q_1 and q_2 have, by their significance, different signs, we may write

$$-\frac{q_1}{T_1} = -\frac{q_2^*}{T_2}$$

and, consequently,

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = \sum \frac{q}{T} = 0,$$

which may be formulated thus: *for the Carnot reversible cycle the algebraic sum of the quotients obtained by dividing the absolute temperatures at which the heat is imparted or extracted into the amounts of heat is equal to zero.*

It is not difficult to prove that this is true of any reversible cycle and not only of the Carnot cycle.

Let us assume that we have a reversible cyclic process of any body of the most general character *abcd* in the *pv* system (Fig. 5-7). By constructing a series of infinitely close adiabatics we break up the cycle into an infinite number of elementary cycles, *efgh*, *fmng*, etc., each of which consists of two adiabatics and two elements of the contour of the given cycle. Since the elements are infinitely small in length, the changes in temperature which they represent will also be infinitely small, so that these elements may be regarded as isotherms. Therefore, each of this infinitely great number of cycles may be regarded as an elementary Carnot cycle. The sum-total of these cycles is equal to the cyclic process *abcd*. Each of the adiabatics (*eh*, *fg*, etc.) cuts the body twice, in opposite directions; the work of expansion on adiabatic, *fg*, in the cycle *efgh* is equal to the work of compression by adiabatic *gf* in the cycle *fmng*, so that in the final analysis the adiabatic processes do not affect the magnitude of the work

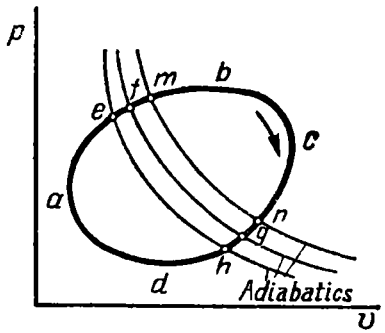


Fig. 5-7

* In the present case the amount of heat q_1 has been given a negative sign and the amount q_2 a positive sign for the following reasons. The amount of heat q_2 is transferred to the cooling agent by means of the working body and, according to the accepted rule, heat transferred to the cooling agent must have a positive sign. The amount of heat q_1 is taken from the source by the working body and for a similar reason must have a negative sign.—*Ed.*

and heat is neither imparted nor extracted during these processes. Therefore, the total action of the elementary cycles is nothing more than the sum of the actions of the elementary process *ef*, *fm*, *ng*, *gh*, etc., that is, it is identical with the cycle shown in the contour *abcd*.

According to the previous paragraph, for each elementary Carnot cycle

$$\sum \frac{dq}{T} = 0,$$

therefore, for the sum of this infinitely great number of elementary cycles, i.e., for the cycle *abcd*

$$\oint \frac{dq}{T} = 0,$$

where $\oint$ is an integral taken for the whole cycle.

If the integral taken for any closed contour is equal to zero, there is, as we know, a corresponding full differential; for reversible processes

$$\frac{dq}{T} = ds \qquad (5\text{-}10)$$

is the full differential of the function s, known as *entropy*, which is determined by the state of the body. And since, for reversible processes, by equation 2-10

$$dq = du + A\,dl,$$

the elementary change in the entropy of the body is

$$ds = \frac{du + A\,dl}{T}. \qquad (5\text{-}11)$$

Since entropy is determined by the state of the body it is perfectly natural that changes in it should be determined fully by the initial and final stages and do not depend on the way in which changes are made.

We know that for the irreversible Carnot cycle we have

$$\eta_t = 1 - \frac{q_2}{q_1} < 1 - \frac{T_2}{T_1};$$

therefore,

$$\frac{q_2}{q_1} > \frac{T_2}{T_1}$$

and

$$\frac{q_2}{T_2} > \frac{q_1}{T_1}.$$

Remembering the unlike signs of q_1 and q_2, we may write

$$\left(\frac{q_2}{T_2}-\frac{q_1}{T_1}\right)>0,$$

or,

$$\sum\frac{q}{T}>0,$$

and for any irreversible cycle

$$\oint\frac{dq}{T}>0.$$

Since

$$\oint\frac{dq}{T}=\oint ds,$$

where the change in entropy is regarded as a change in the entropy of the whole system (i.e., the working body, the source of heat and the cooling agent) resulting from the cyclic process (this will be discussed in detail in 5-12), then for irreversible cycles

$$\oint\frac{dq}{T}=\oint ds>0;$$

for irreversible processes, therefore,

$$ds>0, \tag{5-12}$$

where ds is the elementary change in the entropy of the system.

It must be understood quite clearly that in all cases, both of reversible and irreversible processes, the elementary change in the entropy of a body is

$$ds=\frac{du+A\,dl}{T}.$$

For irreversible processes, in accordance with the explanation in Sec. 2-5,

$$ds=\frac{dq+dq_r}{T}=\frac{dq}{T}+\frac{dq_r}{T} \tag{5-13}$$

where dq_r is the elementary amount of heat connected with the irreversible process.

Applying equation 5-10 we get for reversible processes:

$$\boxed{dq=T\,ds} \tag{5-14}$$

which is the basic equation obtained as a result of the second law of thermodynamics; it may, therefore, be regarded as the analytical expression of that law for reversible processes.

Similarly, for irreversible processes, we get from equation 5-13

$$dq < T\,ds \tag{5-15}$$

which may be regarded as the analytical expression of the second law for irreversible processes.

Since T is always greater than zero, according to equation 5-14, dq and ds in reversible processes have like signs, i.e., the transfer of heat to a body is connected with an increase in its entropy and a transfer of heat from a body with a decrease in its entropy.

In addition to the parameters p, v, t, u and i, therefore, we have a further value describing the state of a body; this new parameter is the entropy, s. It is very difficult for the beginner to grasp the concept of entropy because its physical significance cannot be explained simply or demonstrated visually and because it cannot be measured by any instrument. In one of his investigations, Boltzmann showed by statistical methods that the changes in the entropy of a gas are directly proportional to the natural logarithm of probability and that entropy, therefore, may be taken as a measure of the probability of the state of a gas. For our purposes it is sufficient to regard entropy as a function of the state of the heat, which for any state can be determined by calculation, and the employment of which greatly simplifies both theoretical conclusions and practical calculations. As can be seen from equation 5-10, entropy is measured in the same units as heat capacity, the unit for 1 kg of the body being Cal/kg × deg.

5-7. The Entropy of an Ideal Gas. According to equation 5-11

$$ds = \frac{du + A\,dl}{T},$$

where du = the elementary change in the internal energy of the body;

$dl = p\,dv$, the elementary work of expansion.

Substituting, in the case of an ideal gas, $c_v dT$ for du we get

$$ds = c_v \frac{dT}{T} + A\frac{p}{T}\,dv,$$

and since, according to the characteristic equation $pv = RT$

$$\frac{p}{T} = \frac{R}{v},$$

then

$$ds = c_v \frac{dT}{T} + AR\frac{dv}{v}. \qquad (5\text{-}16)$$

Equation 5-16 gives the increase of entropy accompanying an infinitely small change in the state of the gas as a function of the variables T and v; obviously this increase can be expressed as the function of any pair of the three variables p, v and T, which are connected by the equation of state $pv=RT$, differentiating which we get

$$p\,dv + v\,dp = R\,dT,$$

and dividing by pv we get

$$\frac{dv}{v} + \frac{dp}{p} = \frac{R\,dT}{pv},$$

or

$$\frac{dv}{v} + \frac{dp}{p} = \frac{dT}{T}. \qquad (5\text{-}17)$$

The equation 5-17 which we have obtained is nothing more than the equation of state of an ideal gas in its differential form. Taking from it

$$\frac{dv}{v} = \frac{dT}{T} - \frac{dp}{p}$$

and substituting in equation 5-16, we get

$$ds = c_v \frac{dT}{T} + AR\frac{dT}{T} - AR\frac{dp}{p} = (c_v + AR)\frac{dT}{T} - AR\frac{dp}{p} =$$

$$= c_p \frac{dT}{T} - AR\frac{dp}{p}, \qquad (5\text{-}18)$$

the elementary change in the entropy of a gas as the function of the variables T and p. And if, finally, from equation 5-17 we take

$$\frac{dT}{T} = \frac{dp}{p} + \frac{dv}{v}$$

and substitute this form in equation 5-16, we get

$$ds = c_v \frac{dp}{p} + c_v \frac{dv}{v} + AR \frac{dv}{v} = c_v \frac{dp}{p} + (c_v + AR) \frac{dv}{v} =$$

$$= c_v \frac{dp}{p} + c_p \frac{dv}{v} \qquad (5\text{-}19)$$

which is the increase in entropy as a function of the variables p and v.

Equations 5-16, 5-18 and 5-19 give the entropy increase for an infinitely small change in the state of the gas; the change in entropy for a finite change of state is obtained by integrating these equations within the corresponding limits. If we assume c_p and c_v to be constants we get these results by integration: from equation 5-16

$$s_2 - s_1 = c_v \ln \frac{T_2}{T_1} + AR \ln \frac{v_2}{v_1}; \qquad (5\text{-}20)$$

from equation 5-18

$$s_2 - s_1 = c_p \ln \frac{T_2}{T_1} - AR \ln \frac{p_2}{p_1} = c_p \ln \frac{T_2}{T_1} + AR \ln \frac{p_1}{p_2}; \qquad (5\text{-}21)$$

and from equation 5-19

$$s_2 - s_1 = c_v \ln \frac{p_2}{p_1} + c_p \ln \frac{v_2}{v_1} = c_v \left(\ln \frac{p_2}{p_1} + k \ln \frac{v_2}{v_1} \right) =$$

$$= c_v \ln \frac{p_2 v_2^k}{p_1 v_1^k}. \qquad (5\text{-}22)$$

If, for real gases, the functional dependence of c_p and c_v on the temperature is known, the integration of equations 5-16, 5-18, and 5-19 does not present any difficulties, although the formulas so deduced will be more complicated than 5-20, 5-21 and 5-22. Assuming, that for diatomic gases $c_v = a_v + bt = a_v + b(T - 273) = (a_v - 273b) + bT = a'_v + bT$, where $a'_v = a_v - 273b$, and making the necessary substitution in equation 5-16, we get

$$ds = (a'_v + bT) \frac{dT}{T} + AR \frac{dv}{v} = a'_v \frac{dT}{T} + b\,dT + AR \frac{dv}{v}$$

and, consequently,

$$s_2 - s_1 = a'_v \ln \frac{T_2}{T_1} + b(T_2 - T_1) + AR \ln \frac{v_2}{v_1}.$$

By integrating the differential equations 5-16, 5-18 and 5-19, we get the change in entropy (s_2-s_1) in the process, which is the only thing that is of importance in the majority of thermodynamic calculations, the absolute value of the entropy in the given state having no practical significance.* We can, therefore, compute the entropy s of the gas from any of the states p_0, v_0, T_0, taking $s_0=0$ conditionally, i. e., determine the entropy s of other states as the increase (positive or negative) over this initial state. In that case, for example, equation 5-21 gives us for the state p, v, T,

$$s=c_p \ln\frac{T}{T_0}-AR\ln\frac{p}{p_0}=c_p\ln T-AR\ln p+$$
$$+(AR\ln p_0-c_p\ln T_0)=c_p\ln T-AR\ln p+\text{const},$$

where,

$$\text{const}=AR\ln p_0-c_p\ln T_0.$$

For gases it is usually assumed that $s_0=0$, $p_0=1.033$ ata, and $T_0=273°$ K ($t_0=0°$ C).

Thus, we have six magnitudes characterising the state of a gas: p, v, T, u, i and s; in the case of an ideal gas the first three are related by the equation $pv=RT$, i. e., any two can determine the third and also the relative value of the entropy by equations 5-16, 5-18 and 5-19. As far as the internal energy u and the enthalpy i are concerned, they are, for an ideal gas, functions only of the temperature, T, and can be determined only by using that temperature. Therefore, any two of the six parameters, with the exception of the pairs T and u, T and i and u and i, determine the other four parameters and, therefore, the state of the gas. Each of the values T, u, and i individually determines the other two but not the remaining parameters (p, v, and s) and, therefore, do not determine the state of the gas when they are paired.**

5-8. The *Ts* Heat Diagram. Since every state of a body corresponds to definite values of T and s, these values may be

---

* The exception is provided by the application of thermodynamic equations to chemical processes, i. e., to processes in which the chemical composition of the substance changes. In such cases the absolute value of the entropy is of importance.—*Ed.*

** This later statement applies only to ideal gases. For a real substance any two parameters, including T and u, T and i, and u and i determine its state.—*Ed.*

used to indicate the state graphically; in the general case each value is a point on the curve of the process in a rectangular coordinate system, the values of T being the ordinates and the values of s the abscissae by analogy with the pv diagram. In Fig. 5-8 the curve AB represents a general case of a reversible process depicted in the system Ts, the arrow showing the direction of the process.

With ds infinitely small, the shaded area represents $T\,ds = dq$; therefore area $ABB'A'$, bounded by the curve of the process, the axis of the abscissa and the end ordinates — i.e., the area below the curve — represents $\int_{s_1}^{s_2} T\,ds$, which is the amount of heat q; in the given case the heat q is imparted to the body from an outside source since the process shows an increase of entropy.

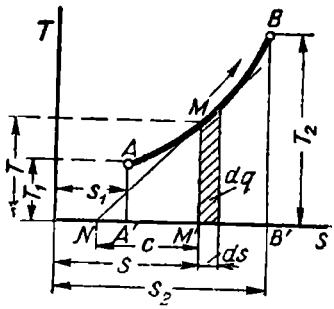


Fig. 5-8

The Ts graph is therefore valuable because it provides, in the form of the area below the curve of a reversible process, the amount of heat q which the body receives from an outside source and retransmits to an outside cooling agent; for this reason it is commonly known as the *heat diagram*. From this diagram it can be seen that the change of entropy as a function of the state is fully determined by the initial and final states of the body, i.e., by the points A and B; the amount of heat q imparted to the body depends on the nature of the process, i.e., it depends on the curve AB.

The subtangent of the process curve in the system Ts gives the value and sign of the weight heat capacity c of this process at the given stage. By the rules of analytical geometry, the value of the subtangent at point M is

$$NM' = T\frac{ds}{dT} = \frac{dq}{dT} = c,$$

the subtangent being positive if it lies to the left of point M', and negative if it lies to the right; in Fig. 5-8 the heat capacity c is positive.

If we draw a horizontal and a vertical through point A, representing a certain state in the system Ts (Fig. 5-9), we

divide the graph into four quadrants; on the basis of what has been said above we may note the following.

Heat capacity $c>0$ corresponds to a change in the state of the body described by any curve from point A through quadrants I and III and, since $c=\frac{dq}{dT}$, dq and dT have like signs, i.e., when heat is imparted to the body its temperature increases; to reduce temperature it is necessary to take heat from the body.

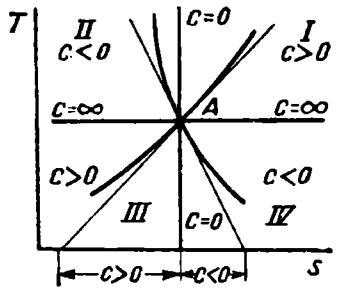


Fig. 5-9

Heat capacity $c<0$ corresponds to a change in the state of the body described by any curve from point A through quadrants II and IV, i.e., dq and dT have unlike signs. Despite the fact that heat is imparted to the body its temperature drops; the temperature increases simultaneously with the extraction of heat from the body. We have given an explanation of these somewhat unusual relations in Sec. 4-6.

The vertical line shows changes in the state of the body when $c=0$ and, therefore, $dq=0$, i. e., heat is neither imparted to nor taken from the body as can be seen from the heat diagram; this is an *adiabatic* process.

The horizontal line shows changes in the state of the body when $c=\infty$; the relation $c=\frac{dq}{dT}$ indicates the same, because for the horizontal in the system Ts we have $T=$const and $dT=0$ while dq does not equal zero; this is an *isothermic* process.

The heat diagram, Ts, therefore, in addition to indicating changes in the temperature and entropy during the process, also shows whether heat has been imparted or extracted, and in what quantity; furthermore, it establishes for any state of the body the true heat capacity, c, of the body. These properties of the heat diagram make it very valuable for thermodynamic investigations and explain why it is as widely applied as the pv diagram.

In irreversible processes, by equation 5-13,

$$ds=\frac{dq}{T}+\frac{dq_r}{T}$$

and, therefore,

$$dq + dq_r = T\,ds, \tag{5-23}$$

and for a finite process

$$q + q_r = \int_{s_1}^{s_2} T\,ds. \tag{5-24}$$

Irreversible processes, however, can only be shown approximately in the Ts and pv diagrams.

5-9. Gas Processes in the *Ts* Heat Diagram. In chapter four we investigated particular ideal gas processes and showed them graphically in a pv diagram. Now let us depict these particular processes in the Ts diagram in the same sequence.

1. *The isochoric process.* When $v = \text{const}$

$$ds = \frac{dq}{T} = \frac{c_v dT}{T}$$

and, therefore,

$$s_2 - s_1 = \int_{T_1}^{T_2} c_v \frac{dT}{T} \tag{5-25}$$

and when $c_v = \text{const}$

$$s_2 - s_1 = c_v \ln \frac{T_2}{T_1} = c_v \ln \frac{p_2}{p_1}. \tag{5-26}$$

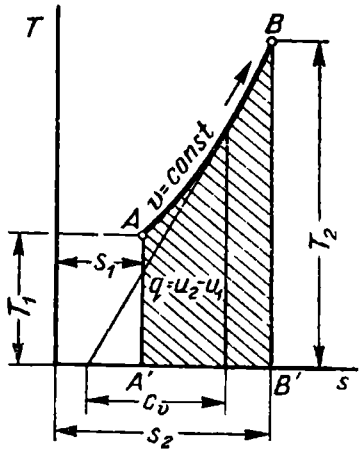


Fig. 5-10

The isochor in the system Ts is the curve AB (Fig. 5-10), concave in shape and rising from left to right (when $c_v = \text{const}$ it is a logarithmic curve); the subtangent to the curve at any point gives the true value of c_v. The isochor has this shape for the following reasons: all the heat imparted to the gas is used in increasing its internal energy, i. e., $ds > 0$ and $dT > 0$; the curve, therefore, rises from left to right. An unchanging subtangent ($c_v = \text{const}$) is possible only if the curve is concave; an increased c_v, depending on temperature, turns the isochor closer to the horizontal but its general shape does not change.

Area $ABB'A'$ under the isochor gives the amount of heat, q, on a certain scale, as well as the change in internal energy $(u_2 - u_1)$.

Since the c_v of an ideal gas is a function of the temperature alone, changes of the entropy in an isochoric process depend exclusively on changes in the temperature (equation 5-25) and do not depend on the volume, i. e., it is identical for all isochors within the given temperature limits. All isochors for the given gas, therefore, are identical and are distributed in pairs equidistantly along the horizontal. This distance between isochors v_1 and v_2, like the change of entropy by the isotherm, is obtained from equation 5-20 when T=const as

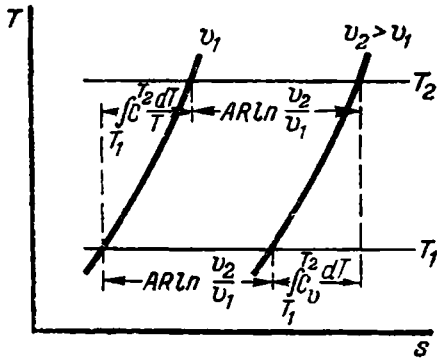


Fig. 5-11

$$s_2 - s_1 = AR \ln \frac{v_2}{v_1}$$

It is, therefore, determined by the relation of the volumes when $v_2 > v_1$ and $s_2 > s_1$, i. e., the greater the volume the farther the isochor is removed from the axis of the ordinate (Fig. 5-11).

2. *The isobaric process.* When p=const

$$ds = \frac{dq}{T} = \frac{c_p dT}{T} \qquad (5\text{-}27)$$

and, therefore,

$$s_2 - s_1 = \int_{T_1}^{T_2} c_p \frac{dT}{T},$$

and when c_p = const

$$s_2 - s_1 = c_p \ln \frac{T_2}{T_1} = c_p \ln \frac{v_2}{v_1}. \qquad (5\text{-}28)$$

The isobar in the system Ts is a curve, AB, (Fig. 5-12) similar to the isochor, i. e., rising from left to right and concave (when c_p=const, the isobar is a logarithmic curve); the subtangent to any point on the curve gives the true value of heat capacity c_p. Since $c_p > c_v$, the isobar in the system Ts is obviously closer to the horizontal than the isochor that passes through the same point. It is worth while noting the relative positions of the isochor and isobar in the Ts and pv

diagrams; in the system pv the isochor is a vertical straight line and the isobar a horizontal straight line, i.e., their relative positions are identical.

The isobar in the system Ts rises from left to right because $c_p > 0$, and it is concave for the same reasons as the isochor.

Area $ABB'A'$ under the isobar gives us, on a certain scale, the amount of heat, q, imparted to the gas, and also the change of enthalpy $(i_2 - i_1)$.

The isobars are identical and equidistant along the horizontal for the reasons given above for the isochors. The distance between any two isobars p_1 and p_2, by equation 5-21, when $T = \text{const}$ is

$$s_2 - s_1 \quad AR \ln \frac{p_1}{p_2}.$$

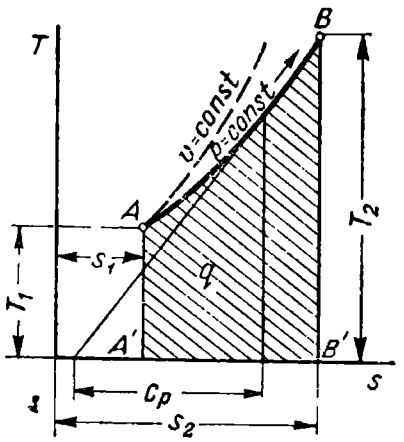


Fig. 5-12

As we see, it is determined by the relative pressures, i.e., it is identical for isobars 1 and 2, 2 and 4, 6 and 12 ata. When $p_1 > p_2$, then $s_2 > s_1$, i. e., the greater the pressure the closer the isobar is to the axis of the ordinate (Fig. 5-13).

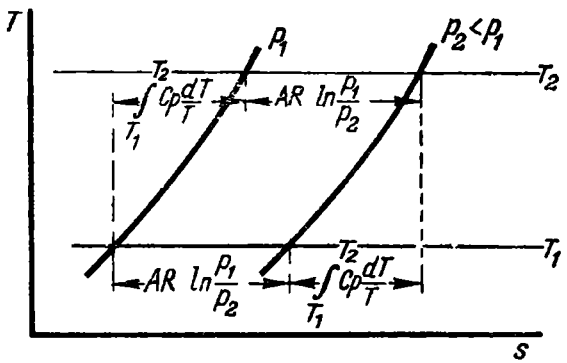


Fig. 5-13

3. *The isothermic process.* According to equation 5-16 for the general case

$$ds = c_v \frac{dT}{T} + AR \frac{dv}{v},$$

whence, when $T = \text{const}$, i.e., $dT = 0$,

$$ds = AR\frac{dv}{v}$$

and, consequently,

$$s_2 - s_1 = AR \ln \frac{V_2}{V_1} = AR \ln \frac{p_1}{p_2}. \qquad (5\text{-}29)$$

The isotherm in the system Ts is a horizontal straight line AB (Fig. 5-14); area $ABB'A'$ gives, on a certain scale, the quantity of heat, q, imparted to the gas and also the work, Al.

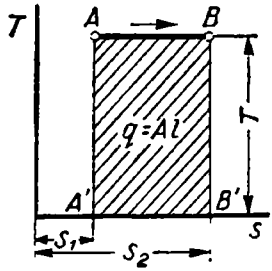


Fig. 5-14

4. *The adiabatic process.* For the adiabatic process $dq=0$ and, therefore, for a reversible process

$$ds = \frac{dq}{T} = 0$$

and

$$\boxed{s = \text{const},} \qquad (5\text{-}30)$$

i.e., the reversible adiabatic process is at the same time an isoentropic process (at constant entropy). In view of this the reversible adiabatic process is shown in the system Ts as a vertical straight line AB (Fig. 5-15); since there is a temper-

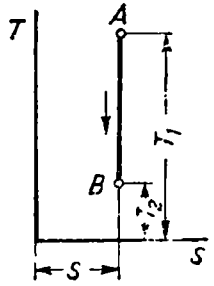


Fig. 5-15

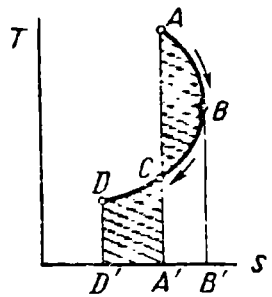


Fig. 5-16

ature drop in the process AB it is a process of expansion (Sec. 4-5). It is obvious from the Ts diagram that in the process AB, dq 0, q 0 and the heat capacity $c=0$.

Using the value of the entropy it is very easy to obtain the equation of the gas adiabatic in the system pv. In the

general case, by equation 5-22, when $k = \text{const}$

$$s_2 - s_1 = c_v \ln \frac{p_2 v_2^k}{p_1 v_1^k},$$

but for the reversible adiabatic process $s_2 = s_1 = \text{const}$, so that

$$\ln \frac{p_2 v_2^k}{p_1 v_1^k} = 0,$$

i.e.,

$$p_2 v_2^k = p_1 v_1^k = p v^k = \text{const},$$

and this is equation 4-23 which we obtained earlier in a more complicated way.

The diagram Ts shows that not every process in which $q = 0$ is adiabatic, as we have already mentioned (Sec. 4-5).

Take, for example, the process $ABCD$ (Fig. 5-16) in which areas ABC and $DCA'D'$ are equal. During the AB element of the process an amount of heat equal to area $ABB'A'$ is imparted to the gas, and during element BCD it gives up an amount of heat equal to area $DBB'D'$; since these areas are equal it is obvious that the result of the whole process $ABCD$ is $q = 0$; the process, however, is not adiabatic, the entropy of the gas changes constantly, at first increasing and then decreasing until, at the end, it is reduced by the distance $D'A'$; the equation of such a process has, of course, nothing in common with the adiabatic equation.

We may again mention the correspondence between the positions of the lines indicating various processes in the pv and Ts diagrams. In the heat diagram the adiabatic is vertical and the isotherm is horizontal; in the pv diagram (Sec. 4-5) we saw that the adiabatic is closer to the vertical than the isotherm, i. e., their relative positions are the same.

In the general case of an irreversible process, by equation 5-13

$$ds = \frac{dq}{T} + \frac{dq_r}{T}$$

and, consequently, for the adiabatic irreversible process, i.e., when $dq = 0$

$$ds = \frac{dq_r}{T} > 0,$$

since $dq_r > 0$ and $T > 0$, i. e., the adiabatic irreversible process is not isoentropic and is always connected with an increase in entropy irrespective of its direction, both in expansion and compression. When there is friction, for example, the adiabatic process is shown only approximately in the system Ts, not as a vertical line but as some curve AB (Fig. 5-17) to the right of the vertical AB_1 of the reversible process within the same limits of change in volume. The adiabatic BC depicts the reverse process of compression, also placed to the right of the vertical BC_1 of the reversible compression. Thus, the direct process of expansion AB and the reverse compression BC are quite different; the reverse process does not result in the gas returning to its initial state at point A, but to a different point, C, with a higher temperature and pressure (since the volume is identical at points A and C). The shaded areas under the adiabatic curves AB and BC show the amount of heat q_r developing inside the gas as a result of friction, and imparted to the gas thus causing higher temperatures at the end of the processes than is the case with reversible processes.

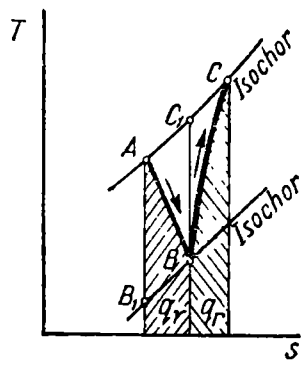


Fig. 5-17

5-10. The Cyclic Process in a *Ts* Heat Diagram. The cyclic process in the Ts system, like that in the pv system, is depicted by a continuous line. Fig. 5-18 is the heat diagram of the reversible cycle $ABCD$, a process of the most general character which the body undergoes in the direction indicated by the arrow (i. e., clockwise). Along the part ABC the body obtains heat from the source, the amount being

$$q_1 = \text{area } ABCC'A'$$

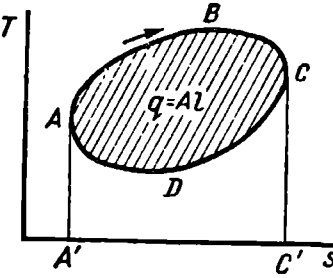


Fig. 5-18

and along the section CDA gives up to the cooling agent the amount of heat

$$q_2 = \text{area } ADCC'A'.$$

The amount of heat transmitted to the body during the cycle,

$$q = q_1 - q_2,$$

as we established in Sec. 5-2, is transformed into the equivalent amount of work of the cycle, l, so that

$$q = q_1 - q_2 = Al = \text{area } ABCD,$$

i. e., as in the pv system, the area of the closed figure of the cycle shows the amount of work done by one cycle, but in heat units (Cal) only; this value is positive if the process follows a clockwise direction (the cycle of a heat engine) and negative if it is counterclockwise (the cycle of a heat pump). Obviously the direction of the cycle in the Ts and pv diagrams is identical.

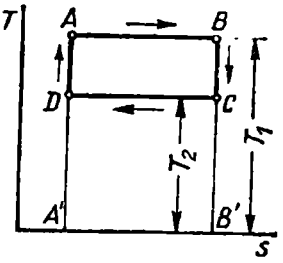


Fig. 5-19

The thermal efficiency of the cycle is

$$\eta_t = \frac{Al}{q_1} = \frac{\text{area } ABCD}{\text{area } ABCC'A'}.$$

It can easily be seen from the Ts diagram that the change of entropy for the full cycle is zero, which is quite understandable because entropy, like the internal energy, is a function of state, and any change, therefore, is fully determined by its values at the initial and final states which, in the case of a full cycle, are identical. It is equally obvious that the efficiency of any cycle is always less than unity because the return of the body from state C to the initial state A is always connected with the loss of a certain amount of heat q_2 which is transferred to the cooling agent, whatever process is carried out; q_2 would be equal to zero only in the case, impossible in practice, of a cycle that followed the contour of the figure $ABCC'A'$ in which the process $C'A'$ takes place with the temperature of the cooling agent at 0° K, i. e., 273° C.* Only in this abstract case would the equation $\eta_t = 1 - \frac{q_2}{q_1}$ be equal to one, i. e., the heat of the source, q_1, would be fully converted into the equivalent amount of work l.

The Carnot reversible cycle, one that consists of two isotherms and two adiabatics, is shown in Fig. 5-19 as a rectangle

* This case is impossible in theory as well as in practice.—*Ed.*

$ABCD$. Earlier, in Sec. 5-2 we obtained the efficiency of the Carnot reversible gas cycle as $\eta_t = 1 - \frac{T_2}{T_1}$, applying the equation $pv = RT$ and assuming that $k = \frac{c_p}{c_v} = \text{const}$. It is clear from the heat diagram that the efficiency of the Carnot cycle does not depend on the nature of the working body, and, consequently, is identical for all bodies and is expressed by $\eta_t = 1 - \frac{T_2}{T_1}$. The isotherm for any body in the system Ts is depicted by a horizontal line and the adiabatic of the reversible process by a vertical line, so that the Carnot cycle is the rectangle $ABCD$ and the efficiency of the cycle is

$$\eta_t = 1 - \frac{q_2}{q_1} = 1 - \frac{\text{area } DCB'A'}{\text{area } ABB'A'} = 1 - \frac{T_2}{T_1}.$$

In the cycle of the general case $ABCD$ (Fig. 5-20) both the transfer of heat to the body by the part of the process ABC and the transfer from the body by the part of the process CDA take place at varying temperatures, but we may speak of some average temperatures T_1 and T_2 as being those at which the heat is transferred to and from the body. We obtain these by constructing the rectangles $MNC'A'$ and $RPC'A'$ equal in area to $ABCC'A'$ and $ADCC'A'$ on the common base $A'C'$. In this case area $MNC'A' = \text{area } ABCC'A' = q_1$, area $RPC'A' - \text{area } ADCC'A' = q_2$ and area $MNPR = \text{area } ABCD = q_1 - q_2 = q = Al$. Thus we obtain the Carnot cycle $MNPR$, which has results identical with those of the cycle $ABCD$; in both cases the body obtains the amount of heat q_1 from outside and has the amount of heat q_2 transferred from it, the body performing the work $Al = q = q_1 - q_2$, so that the efficiency η_t of cycle $ABCD$ is the same as that of the Carnot cycle $MNPR$, η_{t_c}, i. e., $1 - \frac{T_2}{T_1}$. The main difference is that in the Carnot cycle $MNPR$, the heat is transmitted to and taken from the body at the constant temperatures T_1 and T_2, while in the cycle $ABCD$ the temperatures are variables of which T_1 and T_2 are average values. As can

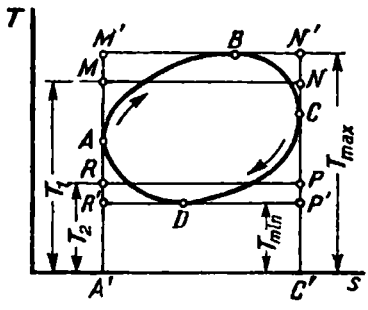


Fig. 5-20

be seen from Fig. 5-20, the work $l>0$ provided $T_1>T_2$, i. e., the average temperature of the source must be greater than the average temperature of the cooling agent, so that the system must always include a body colder than the source of heat—the cooling agent—for heat to be converted into work by the cycle.

As we have already seen in Sec. 5-2, Carnot's reversible cycle is the most advantageous within fixed temperature limits, i.e., it gives the maximum efficiency. The cycle $ABCD$ occurs within the temperature limits T_{max} and T_{min}, (Fig. 5-20) and possesses efficiency

$$\eta_t = 1 - \frac{T_2}{T_1},$$

and the Carnot cycle $M'N'P'R'$ within the same temperature limits possesses efficiency

$$\eta'_{t_0} = 1 - \frac{T_{min}}{T_{max}};$$

but, as we see from the heat diagram, for any contour of the cycle $ABCD$

$$T_2 > T_{min} \text{ and } T_1 < T_{max},$$

and, therefore,

$$\eta_t < \eta'_{t_0}.$$

Since the temperature limits of the cycle are usually fixed in actual heat installations it is natural that the Carnot cycle should be theoretically the most advantageous, since it ensures the maximum economy. It is, therefore, the ideal cycle for any heat engine, although, as we have said, there are a number of reasons why it cannot be fully realised.

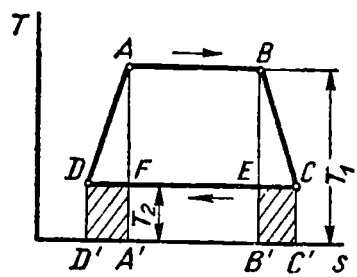


Fig. 5-21

In Sec. 5-2 it was established that the efficiency of the Carnot reversible cycle is always less than $\eta_t = 1 - \frac{T_2}{T_1}$, where T_1 and T_2 are the absolute temperatures of the source of heat and the cooling agent. Fig. 5-21 is a conventional representation of a Carnot cycle, $ABCD$, that is irreversible on account of friction; the adiabatic processes BC and DA take place

under conditions of increasing entropy. The body receives from the source the amount of heat q_1=area $ABB'A'$ and gives up to the cooling agent the amount of heat q_2 =area $DCC'D'$; the work of the cycle, therefore, is

$$Al = q_1 - q_2 = \text{area } ABB'A' - \text{area } DCC'D' = \text{area } ABEF - \\ - (\text{area } DFA'D' + \text{area } ECC'B')$$

But the area $ABEF$ is the work of the Carnot reversible cycle $ABEF$ within the same temperature limits and with the same expenditure of heat by the source, q_1, as in the given irreversible cycle. As a result of the irreversibility of the cycle we have a loss of work which is equal to the sum of the shaded areas. And since the work of the given cycle is less than that of the reversible cycle with the same expenditure of heat q_1, then it is obvious that $\eta_t = \frac{Al}{q_1} < (1 - \frac{T_2}{T_1})$. It must be mentioned that the area of the figure representing the irreversible cycle does not, as we have seen, show the work of the cycle, which is less than that area. It is also of interest to note that it is not necessary to know the character of the irreversible adiabatic processes to determine the work of the cycle and its efficiency, but it is sufficient to know the key points of the cycle A, B, C and D.

5-11. The Regenerative Cycle. As we have seen, the Carnot reversible cycle provides the best use of heat when we have available a source of heat at the constant temperature T_1 and a cooling medium with a constant temperature of T_2, the efficiency of the cycle being

$$\eta_t = 1 - \frac{T_2}{T_1}.$$

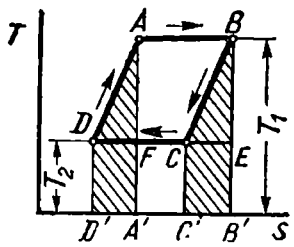


Fig. 5-22

The same efficiency, however, can be obtained from the cycle $ABCD$ in Fig. 5-22, which consists of isotherms AB and CD at temperatures T_1 and T_2 and two horizontally equidistant curves BC and DA, if the system has added to it the so-called *regenerator*, the purpose of which is the reversible consumption of the heat given up by the body during process BC and the reversible imparting of heat to the body during process DA.

Since the curves BC and DA are horizontally equidistant, the shaded areas in Fig. 5-22 are similar:

$$q_{bc} = \text{area } CBB'C', \text{ and}$$
$$q_{da} = \text{area } DAA'D',$$

i.e., the amount of heat is identical in each case but has a different sign.

Under these conditions the work of the cycle is as follows: along the line AB the body obtains heat q_1 from the source, the quantity being measured by area $ABB'A'$, and along the line BC gives up to the regenerator q_{bc} of heat, the quantity being measured by area $CBB'C'$, and to the cooling medium the quantity of heat, q_2, to which the area $DCC'D'$ corresponds; the cycle is completed when the body obtains q_{da} of heat from the regenerator, this being measured by area $DAA'D'$.

Thus, the heat given to the regenerator by the process BC is returned in full to the body during the process DA so that the same amount of heat, q_1, obtained from the source, is expended in this cycle as in the Carnot cycle $ABEF$.

Since the curves BC and DA are horizontally equidistant, $DC=AB=FE$ and, therefore, area $DCC'D'=$area $FEB'A'$, the amount of heat q_2 is the same in the $ABCD$ cycle as in the $ABEF$ Carnot cycle. If the amounts of heat q_1 and q_2 are identical in the two cycles, their work (area $ABCD=$area $ABEF$) and efficiency will also be identical since the efficiency of the cycle $ABCD$ using regeneration is

$$\eta_t = \eta_{t_c} = 1 - \frac{T_2}{T_1}.$$

In its simplest form the regenerator may be regarded as a long, thick-walled pipe with a high heat capacity, the temperature of its walls dropping from T_1 to T_2 in one direction and being constant at any cross-section. During the process BC the working body passes through the pipe to the cooling medium in this direction, i. e., from the hot to the cool end, and gives up q_{bc} of heat, and during the process DA it passes through the pipe in the opposite direction and takes back from it the same amount of heat.

The regenerative cycle was first proposed in 1827 and was later applied to the air engine. The air engine was not widely adopted for a number of reasons but the principle of regeneration is used successfully in modern heat engines and

in metallurgical furnaces; in the latter case the hot gases pass from the furnace through a regeneration chamber and heat up the brick cells of which it is composed. The gases are then passed into a second such chamber and air is passed through the first chamber in the opposite direction and thence into the furnace, its temperature being increased at the expense of the heat obtained from the furnace gases. In more recent times the regenerative principle has been widely applied in steam turbine installations to preheat the water and also in gas turbines.

5-12. Entropy Increase and Degradation of the Energy of an Isolated System. Every process is the result of the interaction of at least two bodies which may be regarded as an isolated, independent system if any sort of extraneous influence is excluded.* It is not difficult to see that in an irreversible process (in which the graph is not a closed figure) the entropy of an isolated system increases. Such an irreversible process, for example, is the transfer of heat Q from a body with a constant temperature T_1 to another body with a constant temperature T_2, T_1 being greater than T_2. In this process the entropy of the first body is reduced by $\frac{Q}{T_1}$ and that of the second increases by $\frac{Q}{T_2}$ so that the entropy of the two bodies changes to the amount of

$$\frac{Q}{T_2}-\frac{Q}{T_1}=Q\left(\frac{1}{T_2}-\frac{1}{T_1}\right)=Q\,\frac{T_1-T_2}{T_1T_2},$$

and since $T_1>T_2$, the value is positive, i.e., the entropy of the system increases.

The same thing occurs in irreversible cyclic processes since in every cycle the final state of the working body is identical with the initial state so that as a result of either a reversible or irreversible cycle the entropy of the working body remains unchanged but the entropy of the system, consisting of the source of heat, the working body and the cooling agent, increases as a result of the increased total entropy of the source of heat and the cooling agent. In the Carnot

* An isolated system is an abstract conception; in actual fact no absolutely isolated system can exist. But the isolated system, like the perfect gas, greatly simplifies the study of a number of processes in thermodynamics.—*Ed.*

reversible cycle the entropy of the source of heat is reduced by $\frac{Q_1}{T_1}$ while that of the cooling agent increases by $\frac{Q_2}{T_2}$ so that the change in the entropy of the system amounts to

$$\frac{Q_2}{T_2} - \frac{Q_1}{T_1}.$$

In the Carnot reversible cycle, as we saw in 5-6, $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$, i. e., the entropy of the system does not change.

Now let us consider a Carnot irreversible process; its efficiency is

$$\eta_t = 1 - \frac{Q_2}{Q_1} < 1 - \frac{T_2}{T_1},$$

where T_1 and T_2 are the constant temperatures of the source of heat and the cooling agent; therefore, for each cycle

$$-\frac{Q_2}{T_2} > -\frac{Q_1}{T_1}, \text{ i. e., } \frac{Q_2}{T_2} > \frac{Q_1}{T_1}$$

which means that

$$\left(\frac{Q_2}{T_2} - \frac{Q_1}{T_1}\right) > 0,$$

and this is the change in the entropy of the system, i. e., it increases.*

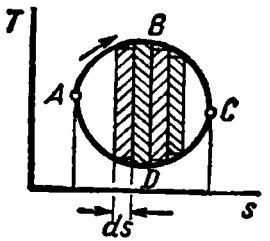


Fig. 5-23

It can easily be seen that entropy increases in any irreversible cycle; actually we can break up any cycle *ABCD* into a series of elemental Carnot cycles in accordance with the shaded areas (Fig. 5-23).

If *ds* is infinitely small the sum of the processes of these elemental cycles will be the same, as we have already established, as that of the given cyclic process. In Carnot irreversible cycles the entropy of the system increases; it therefore increases in the present cycle.

Since all real processes are irreversible, we come to the conclusion that the entropy of an isolated system constantly

* In respect of the sources, Q_2 has a positive sign since the cooling agent receives the heat and Q_1 has a negative sign since the high temperature source gives up the heat. Thus, the increase in the entropy of the cooling agent is greater than the decrease in the entropy of the high temperature source. Since the entropy of the working body that performs the cycle remains unchanged, the entropy of the system increases as a result of the irreversible cycle.—*Ed.*

increases. This entropy increase seems to be connected with the second law of thermodynamics. *Clausius*, studying the universe as an isolated system, made the famous postulate that "*die Entropie der Welt strebt einem Maximum zu*" (*the entropy of the universe strives towards a maximum*). The growth of the entropy in an isolated system is, as we shall now see, connected with a certain *degradation of energy*. A number of examples will prove this.

The amount of heat, Q, given up by a body with a temperature of T_1 can, in a reversible Carnot cycle, perform a maximum amount of work

$$AL = \eta_t Q = Q\left(1 - \frac{T_2}{T_1}\right),$$

where T_2 is the lowest temperature in the given system of bodies. If this amount of heat, Q, is transferred directly to a body with a temperature of $T_1' < T_1$, the amount of work that corresponds to it after its transfer will be

$$AL' = \eta_t' Q = Q\left(1 - \frac{T_2}{T_1}\right).$$

Obviously, since T_1' is less than T_1 the work L' will be less than L, i. e., the transfer of the heat to a lower temperature level involves a loss of work, i. e., a degradation of energy. This loss is

$$AL - AL' = Q\left(1 - \frac{T_2}{T_1}\right) - Q\left(1 - \frac{T_2}{T_1'}\right) = QT_2\left(\frac{1}{T_1'} - \frac{1}{T_1}\right).$$

At the same time the entropy of the system increases as a result of the transfer of the amount of heat, Q, from a body with a temperature of T_1 to a body with a temperature of T_1' by

$$\frac{Q}{T_1'} - \frac{Q}{T_1} = Q\left(\frac{1}{T_1'} - \frac{1}{T_1}\right).$$

Comparing these last two expressions we note that the loss of work is equal to the product of the lower temperature T_2 in the system and the increase in entropy, i. e., it is directly proportional to the increase of entropy.

If the work L in the system of bodies is expended on overcoming friction, converted into its heat equivalent $Q = AL$, then we get an increase in entropy that is equal to $\frac{Q}{T}$ when

the temperature T is constant. This amount of heat, as was formerly the case, corresponds to the maximum work of the Carnot cycle

$$AL' = Q\left(1 - \frac{T_2}{T}\right);$$

thus, as a result of friction, we lose

$$AL - AL' = Q - Q\left(1 - \frac{T_2}{T}\right) = T_2 \frac{Q}{T},$$

i. e., the loss is again equal to the product of the lower temperature T_2 and the increase in entropy.

This relation between the increasing entropy and the decreasing efficiency of a system is common to all irreversible processes. Since the entropy in an isolated system is constantly increasing, it follows that the energy of the system, while remaining unchanged quantitatively, is worsened qualitatively, i. e., there is a degradation of energy, since, in the main, it is transferred to a lower temperature level. All forms of energy, as we have said, are easily converted into heat, which, in its turn, is constantly passing from a body at a higher temperature to one at a lower temperature, thus equalising the temperature of the system. If we follow the example of Clausius and extend the condition outlined above to the whole universe regarded as an isolated system, then we arrive at conclusions that are in sharp contradiction to the materialist conception of world processes. If the entropy of the universe is steadily increasing and its energy suffering degradation, the world process would be working in one direction, that of the degradation of energy, converting it all into heat energy and equalising temperatures; this would exclude the reverse process, the transformation of heat into other forms of energy. The concept of a one-sided world process is inevitably bound up with the concept of the transition of the universe from a definite initial state to an equally definite final state, i. e., with a finite world, one with a "creation" and an "end". Such conclusions, contradictory to our materialist understanding of nature, must be regarded as being without foundation. In the first place, the very idea of an isolated system is abstract and unreal.

There are not, and cannot be, any isolated systems in nature; to a lesser degree than anything else can the universe be regarded as an isolated system since the universe is infinite. A one-sided world process is in direct contradiction to the

dialectical materialist outlook on the world which was formulated exhaustively by Frederick Engels in his *Dialectics of Nature*. Here are some of his postulates: "the whole of nature, ... has its existence in eternal coming into being and passing away, in ceaseless flux, in unresting motion and change; ... the eternally repeated succession of worlds in infinite time is only the logical complement to the coexistence of innumerable worlds in infinite space. ... It is an eternal cycle... that certainly only completes its orbit in periods of time for which our terrestrial year is no adequate measure;" "... matter remains eternally the same in all its transformations, that none of its attributes can ever be lost..."* The irreversibility of natural processes is not, furthermore, a universal law; the very concept of irreversibility is relative. This position was first established by *Boltzmann*, who showed in his classical works that the growth of entropy is a deduction based on the theory of probability. It certainly does not follow from this that processes in which entropy decreases are impossible. According to Boltzmann, every state, however minute its probability, must be repeated. The statistical method for the study of molecular movements, used by Boltzmann, revealed the limits of the applicability of this purely empiric law and dealt Clausius' generalisations a crushing blow. Boltzmann's ideas were later developed and proved by *Smoluchowski* who gave convincing proof of the fact that the irreversibility of processes is a relative concept, that actual processes are irreversible for us only because we limit our examination of them to a finite period of time. If we study processes on a universal scale we find that all of them are reversible in principle.

5-13. Entropy and Probability. As we have said, Boltzmann succeeded in establishing the existence of a definite, regular relation between the entropy of a substance in a given state and the *thermodynamic probability* of that state. Let us examine this in somewhat greater detail. We shall have to begin with a brief review of the concept of *mathematical probability* and that of the *thermodynamic probability* of a state.

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* F. Engels. *Dialectics of Nature*, Foreign Languages Publishing House, Moscow, 1954, pp. 43, 53, 54.

Mathematical probability is the ratio of the number of favourable cases to the number of equally possible cases.

This can be illustrated by an example. Let then be 20 balls in a box, 10 of which are black and 10 red. Let us assume that there is an equal possibility of taking any one of the balls from the box. In the language of the theory of probability, in removing one ball from the box we have 20 equally possible chances. Then what is the mathematical probability that a red ball will be removed from the box?

Since 10 of the balls in the box are red, in removing one of the balls we fulfil the first requirement for which there are, obviously, ten equally possible favourable chances. Therefore, according to our definition, the mathematical possibility that a red ball will be removed from the box is

$$P_r = \frac{\text{number of favourable cases}}{\text{number of equally possible cases}} = \frac{10}{20} = 0.5.$$

We must mention that mathematical probability is always expressed as a fraction since the number of favourable cases is always less than the number of equally possible cases.

Let us, however, continue the example with the balls in a box. Let us assume that five of the ten red balls have a stripe. What then will be the mathematical probability of drawing a red ball with a stripe from the twenty balls in the box?

There are various ways of tackling this simple question. We can immediately determine the number of favourable cases and continue the original mathematical process. Obviously the number of equally possible cases is the same as before, i. e., twenty, the total number of balls in the box, but the number of favourable cases will be equal to the number of striped red balls, i. e., five. The probability of drawing a striped red ball therefore is

$$P_{rs} = \frac{5}{20} = 0.25.$$

There is another way of approaching the solution of this problem. We can first determine the probability of drawing a red ball from the box. We already have the answer to this, i. e., $P_r = \frac{10}{20} = 0.5$. Then we have to determine the probability of the red ball we have drawn possessing a stripe. In this instance the number of equally probable cases will be

the total number of red balls, i. e., 10, and the number of favourable cases will be equal to the number of striped red balls, i. e., 5. Therefore, the mathematical possibility that the red ball drawn from the box (if the case is now regarded as authentic) will have a stripe is $P_s = \frac{5}{10} = 0.5$. If we now multiply the two mathematical probabilities P_r and P_s we get the original mathematical probability P_{rs}:

$$P_{rs} = P_r \times P_s = 0.5 \times 0.5 = 0.25.$$

This last example confirms the general law of the theory of probability, according to which the mathematical probability of a complex case (in our example the probability of drawing a red ball with a stripe) is equal to the product of the mathematical probabilities of the simple cases (in our example: 1—the probability of drawing a red ball and 2—the probability that the red ball will have a stripe) constituting the complex.

Many interesting problems may be solved by the theory of probability. Take the following problem as an example. Three marksmen, *A*, *B* and *C* fire simultaneously, holing the target in two places. It is known that marksman *A* hits the target four times out of five, *B* three times out of four, and *C* twice out of three times. It is required to determine the mathematical probability of *A* and *B* having hit the target and *C* having missed.

The problem is quite a simple one. Let us assume, to begin with, that the results of the contest are not known. Proceeding from this we determine the probability of *B* and *C* hitting the target and *A* missing. From what is given and from our previous example we get the mathematical probability of the complex case as

$$P_A = \frac{3}{4} \times \frac{2}{3} \times \frac{1}{5} = \frac{6}{60}.$$

The mathematical probability that *A* and *C* hit the target and *B* missed will be

$$P_B = \frac{4}{5} \times \frac{2}{3} \times \frac{1}{4} = \frac{8}{60}.$$

And, lastly, the mathematical probability of *A* and *B* hitting the target and *C* missing will be

$$P_C = \frac{4}{5} \times \frac{3}{4} \times \frac{1}{3} = \frac{12}{60}.$$

To return to the data given—A, B and C fired simultaneously but the target was holed in only two places — we may take it as authentic that one of the marksmen missed the target, so that the case of all three hitting it is out of the question. Let P_C' be the mathematical probability that A and B hit the target and C missed, given that the fact of one of the marksmen missing the target is authentic. Obviously $P_C' \neq P_C$. It is also obvious that the mathematical probability P_C', the value of which is to be found, will be greater than P_C by as much as unity is greater than the sum $P_A + P_B + P_C$, since it is authentically known that one marksman missed the target and the mathematical anticipation of authenticity is unity. We can, therefore, write



Fig. 5-24

$$\frac{P_C'}{P_C} = \frac{1}{P_A + P_B + P_C},$$

whence

$$P_C' = \frac{P_C}{P_A + P_B + P_C} = \frac{12 \times 60}{60 \times 26} = \frac{6}{13}.$$

Now let us look at an example that is directly related to thermodynamics. Let it be assumed that in a vessel which we divide mentally into two equal parts there is one molecule in a state of chaotic heat movement* (Fig. 5-24). What is the mathematical probability that at the given moment the molecule will be in the left-hand half of the vessel? Since it is given that the left- and right-hand halves of the vessel are equal and that it is equally possible for the molecule to be in either half of the vessel, the fundamental mathematical anticipation is

$$P_1 = \frac{1}{2}.$$

If there were two molecules instead of one in the vessel the mathematical probability of the two molecules being in one and the same half, say the left-hand half, of the vessel

* Strictly speaking, such concepts as heat, temperature and other "statistical" values only have a meaning in connection with systems that consist of a very large number of molecules.

should be

$$P_2 = \frac{1}{2} \times \frac{1}{2} = \left(\frac{1}{2}\right)^2.$$

By analogy we should get $P_3 = \left(\frac{1}{2}\right)^3$ for three molecules and $P_4 = \left(\frac{1}{2}\right)^4$ for four molecules, etc. If there are N molecules in the vessel the mathematical probability of their all being in one half of the vessel would be $P_N = \left(\frac{1}{2}\right)^N$. Since N is always a very big number, the mathematical probability of P_N would be a very small number* and, consequently, there is little probability of a spontaneous increase in the pressure of one half of the vessel.

This last example is particularly instructive. Among the many formulations given for the second law of thermodynamics there is the following: *spontaneous processes are irreversible.* From this formulation it follows that processes taking place "of their own accord", among which we may include the diffusion of gases, the transfer of heat from a warmer to a colder body with a final difference of temperatures, the expansion of gas without the aid of external work, etc., are one-way processes. It is well known that the process of separating the gases of a mixture (the opposite of diffusion) never takes place "of its own accord", that is, it never takes place without additional, *compensating processes*; we imagine it to be highly improbable, for example, that the air in some vessel should suddenly spontaneously separate into nitrogen and oxygen. Equally improbable is the transfer of heat from a cooler body to a warmer body or the spontaneous compression of a gas.

As we have said above, entropy increases as a result of an irreversible process in an isolated system. If it were possible to carry out an irreversible process in the opposite direction the entropy could be expected to decrease. This, however, is impossible in practice.

We may add the following to what has been said. The mathematical probability of a process functioning spontaneously towards a decrease in entropy in the isolated sys-

* We must remind the reader that a mol of gas contains about 6×10^{26} molecules. Consequently, the mathematical probability of all the molecules gathering in half the volume at their disposal would be impossibly small: $P_N \approx 10^{-1.2-10^{26}}$.

tem under discussion is so remote that such processes are never realised "of their own accord" in practice. We convinced ourselves of this by determining the mathematical probability of the spontaneous compression of a gas.

In view of what has been said we may put forward the proposition that there is some sort of mutual relation between entropy and probability. We shall now not only prove for ourselves the justice of this assumption but shall even determine the character of this relation.

But before we study this question we must acquaint ourselves with the concepts *macroscopic* and *microscopic* states and with *the thermodynamic probability of state.*

The *macroscopic* state (*macrostate*) of a system is determined by its parameters — pressure, temperature, specific volume, internal energy, etc. Since, in principle, it is necessary to know only two of them to determine all the others, the macrostate of a system may be determined by any two thermodynamic parameters, for instance v and u. When we spoke of the *thermodynamic state* of a system or simply of the state of a system in earlier chapters, we had in view the macrostate.

The *microscopic* state (*microstate*) of a system is determined by the whole set of parameters defining the state of each of the molecules in the system: velocity, position in space, etc. It is incorrect, therefore, to regard the microstate as being the state of any molecule. We repeat—the microstate is determined by the sum-total of all the parameters of all the molecules of the system.

It is important to note that a very great variety of microstates may correspond to one macrostate. Let us take a simple example. Let there be available a system constituting a gas at rest in a rigid vessel. Let it be assumed, as we said above, that the macrostate of the system can be determined by the values of v and u. The unchanging internal energy of the system, however, does not determine the character of the distribution of energy between the various molecules, i. e., does not determine the microstate of the system. The given macrostate may have a corresponding microstate in which all the molecules of the system possess the same quantity of energy, the sum of which is equal to the internal energy of the system. But there may also be other microstates that correspond to the same macrostate. It may be assumed, for example, that one half of

the molecules possesses double the amount of energy possessed by the other half; but if all the molecules are well mixed and the sum-total of their energy is, as was formerly the case, equal to the internal energy of the system, the new microstate will correspond to the same macrostate.

Thus, proceeding only from the distribution of energy between the individual molecules it may be established that a large number of different microstates correspond to the same macrostate.* At the same time it must be borne in mind that differences in microstates are not always determined by different distributions of energy among the molecules. There are other causes of this difference in microstates, the distribution of the molecules in space, for example.

It is also important to remember that an unchanging macrostate does not by any means ensure an unchanging microstate. As a consequence of the chaotic movement of the molecules and the constant collisions between them, there is a definite distribution of energy among the molecules for every moment in time and, naturally, a definite microstate. And since *no one microstate is in any way superior to the others* there is a constant change of microstates. In principle, of course, it is possible that a microstate might be attained that corresponds to some new macrostate differing from the previous one. It is possible, for example, that the molecules concentrated in one half of a container should possess greater energy than those in the other half. This would result in a new macrostate with a higher temperature in one part of the gas than in the others.

It must not, however, be thought that there must necessarily be a change in the macrostate as a result of the constant changes in the microstate of a system (e. g., of a gas). To the outside observer who can only note changes in the thermodynamic parameters it will seem that the system maintains a state that is completely unchanging.

Now we come face to face with the concept of the thermodynamic probability of the state of a system. *Thermodynamic probability*, or *the statistical weight of the macrostate*,

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* According to the quantum theory of energy, the energy of any body is made up of small but finite portions of energy that are not further divisible. Therefore, the number of microstates that realise one and the same macrostate, although enormous, is finite.

is the number of microstates that can realise the given macrostate.

This will obviously differ from mathematical probability which is always expressed by a fraction, because thermodynamic probability is expressed by a whole number, usually a very big one.

If a spontaneous process takes place in an isolated system and the macrostate is changed as a result of it, this means that the new macrostate will have a greater number of microstates than the previous one. It is, therefore, clear that the thermodynamic probability of the system increases as a result of the spontaneous process. It was precisely from this point of view that Boltzmann produced his formulation of the second law of thermodynamics: *nature strives from less probable towards more probable conditions.*

The increase of entropy in an isolated system in irreversible, spontaneous processes and the simultaneous increase in the thermodynamic probability of the state of the system give us every reason to assume that entropy and thermodynamic probability are related values:

$$S = \varphi(P).$$

We determine the relation between entropy and thermodynamic probability in the following way.

Let there be two systems possessing entropy S_1 and S_2 respectively; let their thermodynamic probability be P_1 and P_2. And let these two systems have a total entropy S and a total thermodynamic probability P. Entropy, like all caloric parameters, is additive, thus

$$S = S_1 + S_2.$$

The thermodynamic probability of the combined system will be:

$$P = P_1 \times P_2.$$

The last equation follows from the fact that every microstate of one of the systems jointly with any microstate of the other system gives the microstate of the joint system. The number of microstates of the joint system that can produce one and the same macrostate, that is, the thermodynamic probability of the joint system, will be equal to the number of all possible combinations, that is the product of the thermodynamic probabilities of the two systems.

Since the entropy of each system is related to thermodynamic probability by the same function $S_1=\varphi(P_1)$, $S_2=\varphi(P_2)$ and $S=\varphi(P)$ and we may write the equation as

$$\varphi(P_1\times P_2)=\varphi(P_1)\times\varphi(P_2).$$

Differentiating this equation for P_1 we get

$$\varphi'(P_1\times P_2)\times P_2=\varphi'(P_1)$$

and differentiating for P_2,

$$\varphi''(P_1\times P_2)\,P_1\times P_2+\varphi'(P_1\times P_2)=0.$$

Or, since $P_1\times P_2=P$,

$$\varphi''(P)\times P+\varphi'(P)=0.$$

Thus, we get a differential equation of the second degree in which the unknown is the function itself. The solution of such an equation presents no great difficulty.

It is known that

$$\varphi''(P)=\frac{d\varphi'(P)}{dP}$$

so that our differential equation may be written

$$\frac{d\varphi'(P)}{dP}\times P+\varphi'(P)=0,$$

or,

$$\frac{d\varphi'(P)}{\varphi'(P)}+\frac{dP}{P}=0.$$

Integrating this expression, we get

$$\ln\varphi'(P)+\ln P=\text{const},$$

or,

$$\varphi'(P)\times P=\text{k}.$$

But,

$$\varphi'(P)=\frac{d\varphi(P)}{dP}$$

and we may, therefore, write

$$\frac{d\varphi(P)}{dP}\times P=k,$$

or

$$d\varphi(P)=k\frac{dP}{P}.$$

Integrating this we get

$$\varphi(P) = k \ln P + k_1.$$

Since $\varphi(P) = S$ we may write

$$S = k \ln P + k_1.$$

One of the constants of this last equation, k_1, is easily determined. In view of the fact that $S = S_1 + S_2$ and $P = P_1 \times P_2$ we may write

$$k \ln P_1 \times P_2 + k_1 = k \ln P_1 + k_1 + k \ln P_2 + k_1,$$

from which it follows that $k_1 = 0$, and, therefore, we get the final equation:

$$S = k \times \ln P. \tag{5-31}$$

In order to obtain the constant k we must make an intricate calculation based on quantum statistics. We cannot reproduce these calculations in this book and will confine ourselves to saying that the constant k has been found and is none other than the Boltzmann constant with which we are already familiar, the universal gas constant computed for one molecule of gas. Its value is determined by

$$k = \frac{A\mu R}{N_\mu} \approx 3.28 \times 10^{-27} \text{Cal/°K}. \tag{5-32}$$

Let us now again imagine the vessel in Fig. 5-24 that we divided mentally into two equal parts and filled with a gas possessing the properties of a perfect gas. As far as the distribution of the molecules between the two parts of the vessel is concerned*, it must be said that the most probable case is one in which the molecules are equally divided between left- and right-hand parts of the vessel. Nevertheless, the actual case in which the number of molecules in the two parts is exactly the same will be relatively rare. Because of the chaotic heat movement of the molecules the number of them, in the left-hand half, for example, will be constantly changing and the presence of exactly half the molecules in that half of the vessel will be only an average condition.

It must be borne in mind that the number of molecules in the left-hand part of the vessel will always be close to

* It is assumed, of course, that the number of molecules is very great.

half the total number; therefore the probability of the actual distribution of the molecules over two equal parts of the vessel will always be close to the maximum probability of equal distribution although it will not reach that maximum (it will be somewhat short of maximum).

The theory also enables us to determine the scale of the deviation from the most probable state. It has been shown that the magnitude of the deviation will be in accordance with the law of $\sqrt{N}$. As applied to the present case this has the following significance.

Let us suppose that the vessel contains only 200 molecules. In one half of this vessel there should be an average of 100 molecules. The deviation from this average number will be:

$$\Delta N = \pm\sqrt{N} = \pm\sqrt{100} = \pm 10.$$

Thus the deviation will, as a rule, not be more than 10% of the average value. This big percentage of deviation was obtained by making the number of molecules in the vessel very small.

If we assume that there are not 200 but 20,000 molecules, ΔN will amount to ± 100 molecules or 1%. If the number of molecules in the vessel is 2×10^{20} (which is considerably less than the number of molecules in a mol!), the deviation would not be greater than 10^{10} molecules which is only 10^{-8}%. In the last mentioned case the deviation from the state of equal distribution would not be felt.

Let us assume that we have at our disposal a gas that is absolutely isolated from the surrounding medium and is, therefore, an isolated system. In the course of time this closed system must reach equilibrium; the entropy of the isolated system should in that case reach the maximum.

In this case, however, there will be some degree of vacillation about the state of equilibrium which is known as *fluctuation*. As we know from equation 5-31, the maximum value of entropy corresponds to a maximum value of thermodynamic probability. Obviously the state of the system that is realised through fluctuation should differ from the state of equilibrium by a minimum value of entropy and a minimum value of thermodynamic probability. Every such state is the more easily realised the closer its thermodynamic probability is to that of equilibrium.

The relative value of possible fluctuations is the greater the less the size of the system being studied. This can be convincingly demonstrated by means of the calculations carried out by physicists. Let us assume that we mentally extract one cubic centimetre of air from the surrounding atmospheric medium. How long must we wait for a change in the density of this air, due to fluctuation, to the extent of only 1%? Calculations have shown that the observer would be able to note this phenomenon if his observations were carried on for the enormous period of 10^{140} years. But if the cube of air which we mentally separate from the atmosphere is only 0.008 of a cubic micron, the 1% change in density would then take place much more frequently—about a thousand million times a second.

Can we, in practice, observe the changes in thermodynamic parameters that are due to fluctuation?

All that has been said above indicates a negative answer to this question. A simple calculation will convince us of this. Let S_m and P_m be the entropy and thermodynamic probability of a state of equilibrium, and S and P the entropy and thermodynamic probability of a state attained as a result of fluctuation. Obviously we may write the equation

$$S_m - S = k \ln \frac{P_m}{P} = 2.303 \times k \log \frac{P_m}{P},$$

whence we get

$$\frac{P_m}{P} = 10^{\frac{S_m - S}{2.303 \times k}}.$$

Let us assume that we are still able to measure a difference in the entropy of the system that is equal to 10^{-6} Cal/°K*. In view of the fact that $k = 3.28 \times 10^{-27}$ Cal/°K, we get

$$\frac{P_m}{P} = 10^{\frac{10^{-6}}{2.303 \times 3.28 \times 10^{-27}}} > 10^{200}.$$

Deviation from the state of equilibrium with such a tremendous ratio of probability is so improbable that it would not be possible to observe it in practice. This is the more true in view of the fact that if a system ever did attain this

* Actually it is impossible to measure such a small difference in entropy; the possible error in measurement is greater than the value to be measured.

state it would be for such a brief period of time that no instrument could register it.

Therefore, a system that is in a state of thermodynamic equilibrium is constantly oscillating about that state. The magnitude of the oscillations (the deviations from the state of equilibrium) are so insignificant that it is practically impossible to observe them. As far as using fluctuations for practical purpose is concerned, this is not only impossible in practice but also theoretically.

The statistical interpretation of the essence of entropy and of the second law of thermodynamics was a step forward in explaining the physical meaning of natural phenomena. Using the statistical explanation of the second law as a basis, Boltzmann showed that in principle no system can be in a state of *complete* equilibrium since there must always be fluctuation.

The second law of thermodynamics is applicable only to macroscopic systems, that is, systems consisting of a great number of particles. The principle of increasing entropy in irreversible processes is true only in respect of isolated macroscopic systems. It is, therefore, unscientific and profoundly erroneous to attempt the extension of this principle to the universe, since the latter is boundless and has existed infinitely long.

5-14. Reversibility and the Performance of Work. An isolated system can only perform work when it is not in a state of complete equilibrium. If we exclude chemical processes from our study, then, for an isolated system to perform work, the pressures or temperatures of the bodies in the system under discussion must not be absolutely identical. In the first case, i. e., that of the bodies in the system having different pressures, we say that the system does not possess mechanical equilibrium. In the second case, i. e., when the bodies in the system possess different temperatures, we say that the system does not possess thermal (heat) equilibrium. A system is therefore able to perform work when it is either mechanically or thermally out of equilibrium (or unbalanced in the mechanical or thermal sense).

It is obvious that as work progresses an isolated system will approach the state of equilibrium.

Let it be assumed that the isolated system consists of a surrounding medium, the temperature and pressure of which

is for all practical purposes unchanging, and of compressed air which is at the same temperature as the surrounding medium. Such a system is in a state of thermal equilibrium (the temperatures are identical) but is in an unbalanced mechanical state (the pressures differ). Such a system can perform work. The work may, for example, be done by an ordinary piston engine actuated by compressed air. The work can continue until the compressed air has been used up. After this the pressure of all the bodies of the system will be identical, or, in other words, there will not be that mechanically unbalanced state without which the further performance of work is impossible.

If we have a system with two sources of heat at different temperatures and a working body whose initial state is of no importance, we have a thermally unbalanced system that can perform work, for instance, by the working body repeating the Carnot cycle. The Carnot cycle results in a certain amount of work having been performed and also in the transfer of a definite amount of heat from the high-temperature to the low-temperature reservoir. A further result is that the temperature of the hotter body is reduced and that of the cooler body raised.* In the course of time the temperature of the two bodies equalises, the system attains thermal equilibrium and any further work is impossible.

The performance of work by an isolated system, therefore, is only possible by the transition of the system from an unbalanced to a balanced state. The magnitude of the work, as we know, depends on the nature of the process. From this it follows that it is not a matter of indifference, as far as the work is concerned, how the transition from the unbalanced to the balanced state is made.

Let us again assume that we have a thermally unbalanced system consisting of two sources of heat at different temperatures and a working body. We can easily imagine a situation in which the heat of the hotter body is transferred to the cooler without the aid of the working body. The result of such a process would be that the temperatures of all the bodies of the system would, in the course of time, equalise and the system would be in a state of thermal equilibrium without any work of any sort having been

* This is true only if we assume infinitely great sources of heat. If this assumption is made the transfer of heat in finite quantities to or from a source does not change its temperature.

done.* Such a process of heat exchange (the equalising of the temperatures) without the performance of work must take place at a finite difference of temperature, i. e., it is irreversible. On the contrary, the maximum work during the passing of a system from an unbalanced state to equilibrium is obtained as a result of the working body repeatedly completing the Carnot cycle during which the highest temperature of the working body is equal to that of the source of heat, and the lowest temperature is equal to that of the cooling agent, i. e., as a result only of processes that are fully reversible.

If we have a mechanically unbalanced isolated system which, as before, consists of a supply of compressed air and a medium, again the maximum amount of work during the transition from the unbalanced state to equilibrium will be obtainable from processes that are fully reversible. Let us suppose that the work is performed by a piston engine. It is obvious, all other conditions being equal, that the less the friction between the piston and the cylinder wall, the greater the amount of work obtained. Friction, however, gives rise to a typical irreversible process. The greatest amount of work would be obtainable if there were no friction at all, i. e., by a fully reversible process.

Thus, we come to the following important conclusions:

1. An isolated system is capable of performing work only when it is not in a state of balance. Once equilibrium has been attained the ability of the system to perform work is exhausted.

2. In order to obtain the greatest amount of work from a system during its transition from an unbalanced to a balanced state it is essential that all the processes involved be reversible.

It is very important to be able to calculate the maximum amount of useful work** that a system can perform, or, as it is sometimes put, to determine the system's ability to perform work. Let it be assumed that we have a closed system consisting of the surrounding medium, and some body or

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* For the sake of simplicity we may assume that the temperature of the working body does not change at all having been initially equal to the temperature of the thermal equilibrium of the system.

** By *useful* work we mean that part of the work performed by the system that we can use for our own purposes.

bodies having a pressure p and a temperature T (or any one of those parameters) that differ from those of the medium.

From now on we shall call this body or group of bodies *the source of work.*

We shall also assume that the temperature T_0 and the pressure p_0 of the surrounding medium are unchanging or, at least, do not depend on whether heat is imparted to or taken from the medium. Since, in the general case, $p \neq p_0$ and $T \neq T_0$ the closed system is unbalanced and, consequently, capable of performing work. Let us attempt to determine the maximum useful work of the system, or its ability to perform work. For this purpose let us introduce the following values: let U_1 and V_1 be the internal energy and volume of the source of work in its initial state, that is, unbalanced in respect of the surrounding medium; let U_2 and V_2 be the internal energy and volume of the source of work in its final state of equilibrium in respect of the surrounding medium. As we have already said, the initial pressure and temperature are p and T and the final (also those of the medium) p_0 and T_0. Let U_{01} be the initial internal energy of the medium and U_{02} its final internal energy. Thus, the total internal energy of the system U' in its initial unbalanced state must be:

$$U' = U_1 + U_{01},$$

and the total internal energy at the final, balanced state must be:

$$U'' = U_2 + U_{02}.$$

Since it is given that the system under consideration is a closed system in which there is no exchange of heat with any outside bodies, the work can be performed by the system only by the expenditure of its internal energy:

$$AL = U' - U''$$

or, applying the above equations,

$$AL = (U_1 - U_2) + (U_{01} - U_{02}). \qquad (5\text{-}33)$$

However, an exchange of heat may take place between the source of work and the surrounding medium; the source of work, furthermore, may perform work on the medium (against the pressure of the medium). If Q_0 is the amount of heat imparted by the source of work to the medium and

L_0 is the work performed by the source on the medium, we may write

$$U_{02} - U_{01} = Q_0 + AL_0.$$

Since the pressure p_0 of the medium is constant

$$L_0 = p_0 (V_2 - V_1)$$

so that

$$U_{01} - U_{02} = -Q_0 - Ap_0 (V_2 - V_1). \qquad (5\text{-}34)$$

Taking the value of $U_{01} - U_{02}$ from equation 5-34 and substituting it in equation 5-33, we get

$$AL = (U_1 - U_2) - Q_0 - Ap_0 (V_2 - V_1). \qquad (5.35)$$

The amount of heat imparted to the medium, Q_0, is obviously equal to the product of the constant temperature of the medium T_0 and the increase of the entropy of the medium $(S_{02} - S_{01})$, i. e.,

$$Q_0 = T_0 (S_{02} - S_{01}). \qquad (5\text{-}36)$$

Taking the value of Q_0 from equation 5-36 and substituting it in equation 5-35 we get

$$AL = (U_1 - U_2) - T_0 (S_{02} - S_{01}) - Ap_0 (V_2 - V_1). \qquad (5\text{-}37)$$

Equation 5-37 gives the amount of useful work performed by the system during its transition from an unbalanced to a balanced state, since that part of the work expended on the compression of the medium $p_0(V_2 - V_1)$ which we cannot use for our own purposes has been deducted. Equation 5-37, however, still does not give us the magnitude of the maximum amount of useful work because it does not provide conditions for the essential reversibility of all the processes taking place in the system.

To obtain the equation of *maximum useful work* we must apply the following postulate: *processes taking place in a closed system do not change the entropy of that system.** Since the closed system under discussion consists only of a source of work and a medium, and since, in accordance with what has been said above, the entropy of the medium increases by the amount $S_{02} - S_{01}$, the entropy of the source of work must be reduced by a similar quantity. Let S_1 be the entropy

* As the reader will remember, the entropy of a closed system increases as the result of irreversible processes.

of the source of work in its initial, unbalanced state and S_2 the entropy of the source of work when the system is in its final state of equilibrium; thus we may write

$$S_{02} - S_{01} = S_1 - S_2. \qquad (5\text{-}38)$$

This last equation is true only of reversible processes. Taking into consideration equations 5-38 and 5-37 we may now evolve the expression for the maximum useful work of the system (L_w=useful work):

$$A\,(L_w)_{max} = (U_1 - U_2) - T_0\,(S_1 - S_2) - Ap_0\,(V_2 - V_1). \qquad (5\text{-}39)$$

Now let us look at some concrete examples. In Fig. 5-25 point *1* is the initial state of a source of work*; point *0* represents the parameters of the medium p_0, T_0. As we see from Fig. 5-25 points *1* and *0* lie on one isotherm (the isotherm of the medium) so that in its initial, unbalanced state the closed system, consisting of a source of work and a medium, is in a state of thermal but not mechanical equilibrium ($p_1 > p_0$). What is the maximum useful work that may be performed by this system? This simple problem may be solved directly by equation 5-39 or with the aid of the *pv* diagram in Fig. 5-25. Using the *pv* diagram we see that the system's ability to perform useful work is exhausted when the source of work has passed from state *1* to state *0*, i. e., when the isolated system has attained a state of equilibrium. For the maximum amount of work to be performed it is essential that the transition of the source of work from state *1* to state *0* should be a fully reversible process. We must, therefore, first determine the possible reversible process (or sum of reversible processes) for the transition of the source of work from *1* to *0*.

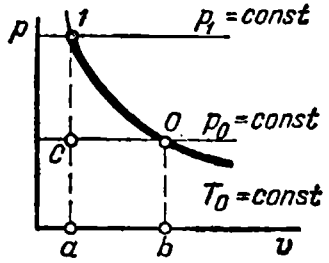


Fig. 5-25

Since the isolated system under discussion includes only one source of heat with a constant temperature, i. e., the medium, the reversible process may be regarded either without an exchange of heat between the working body and the medium (the adiabatic expansion or compression of the

* For the sake of simplicity we shall assume that the source of work possesses the properties of an ideal gas.

source of work) or with an exchange of heat between them, but with the proviso that the temperature of the medium T_0 remains unchanged (the isothermic expansion or compression of the source of work at the temperature T_0). It is easy to realise that in all other processes it is inevitable that there should be an exchange of heat between the source of work and the medium with a finite difference in temperature, in which case the realisation of a *reversible* process would be impossible in principle. This means that the only possible reversible process between state *1* and state *0* is the expansion of the gas according to the isotherm T_0. The amount of work performed by the source during this process will be equal to area *1-0-b-a* (Fig. 5-25).

The whole of this amount of work cannot be used for our own purposes, an amount equal to area *a-c-0-b* must inevitably be expended on compressing the medium (work performed against the constant pressure of the medium p_0). Therefore the maximum possible useful work is equal to the difference between the total amount of work performed and the amount expended on compressing the medium—it is the equivalent of area *1-0-c*.

It is easy to obtain the same result from equation 5-39*. Since the source of work possesses the properties of an ideal gas, and since the temperature of the source at states *1* and *0* is similar and equal to T_0, the internal energy of the source of work at states *1* and *0* will also be the same, and the first member of equation 5-39 will be equal to zero. The second member of equation 5-39 is the amount of heat imparted to the source of work in the isothermic process at the temperature T_0. Since the source of work possesses the properties of an ideal gas the amount of heat imparted during the isothermic process will be equal to the work of that process (the internal energy remains unchanged!). The entropy of the source of work increases in the process of isothermic expansion (heat is imparted!), $S_0 > S_1$, so that the second member of equation 5-39 will be positive. The numerical value of this member will be the equivalent of area *1-0-b-a* in Fig. 5-25. The last member of the equation will be negative ($V_2 > V_1$) and its numerical value will be the equivalent of area *a-c-0-b*. Thus,

$$A(L_w)_{max} = \text{area } 1\text{-}0\text{-}b\text{-}a - \text{area } a\text{-}c\text{-}0\text{-}b = \text{area } 1\text{-}0\text{-}c.$$

* In equation 5-39 exponent 2 must be changed to exponent 0.

Now let us look at a second example. Let us assume that the closed system consists, as before, of a source of work possessing the properties of an ideal gas and a medium. The initial state of the source of work is shown by point *1* in the *pv* diagram in Fig. 5-26.

Point *0* again represents the state of the source of work at a temperature and pressure equal to those of the medium, i. e., the source of work is in a state of equilibrium with the medium. We must first determine a possible reversible path for the transition of the source of work from state *1* to state *0*. As we have said, the only possible reversible processes in a system containing one single source of heat with unchanging temperature (the medium with a temperature of T_0) are the adiabatic and the isothermic process at temperature T_0. Therefore the only possible way for the source of work to be converted from state *1* to state *0*, where it is in equilibrium with the medium, is by its adiabatic expansion from the initial state to the temperature of the medium (adiabatic *1-a* in Fig. 5-26) and its further compression at constant temperature T_0 (isotherm *a-0* in Fig. 5-26).

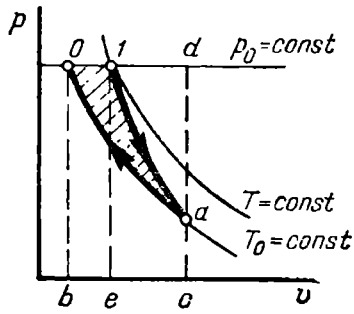


Fig. 5-26

What will the maximum useful work amount to? As before, this problem can be solved in two ways—directly, by the application of equation 5-39, in which the exponent 2 is changed to exponent 0, or with the aid of the *pv* diagram in Fig. 5-26. Let us first take the second method. Since, in the process of adiabatic expansion, *1-a*, the pressure of the source of work will all the time be less than that of the medium, p_0,* the gas, during this process, performs work equivalent to area *1-a-c-e*, which is less than the work equivalent to area *1-d-c-e*, required to compress the medium. It therefore follows that in this case, not only can no useful work be performed, but, on the contrary, work equivalent to area *1-d-a* must be expended to carry out the process *1-a*. We may imagine that the work necessary for this process is

* Excluding the initial point *1*, at which the pressure of the source of work is equal to the pressure of the medium, *p*.

taken temporarily from some source extraneous to the system under discussion. The process of isothermic contraction requires work equal to area *a-0-b-c*. This work can be performed by a medium whose pressure p_0 is always greater than that of the source of work.* The work that can be performed by the medium through a reduction in the volume of the working system corresponding to the isothermic compression *a-0*, is, moreover, greater than the work that must be expended on the compression of the source of work by an amount equal to area *d-a-0*. Obviously the required value of the maximum useful work will equal the difference between the surplus work, the equivalent of area *d-a-0*, and the work borrowed previously from an outside source, the equivalent of area *1-d-a*, that is,

$$(L_w)_{max} = \text{area } d\text{-}a\text{-}0 - \text{area } 1\text{-}d\text{-}a = \text{area } 1\text{-}a\text{-}0.$$

As in the previous example, the value of $(L_w)_{max}$ may be determined directly from equation 5-39; this equation can be written as follows in the present case

$$A(L_w)_{max} = (U_1 - U_0) - T_0(S_1 - S_0) - Ap_0(V_0 - V_1). \quad (5\text{-}40)$$

The first member of the equation, $U_1 - U_0$, represents the work of adiabatic expansion between the temperatures T_1 and T_0 irrespective of the value of the initial and final pressures.** This work will be positive and will be equivalent to area *1-a-c-e*.

The second member of equation 5-40 represents the amount of heat imparted to the medium by the source of work. Since the entropy of the source of work does not change during the adiabatic expansion *1-a*, $S_1 = S_a$ and, consequently,

$$T_0(S_1 - S_0) = T_0(S_a - S_0).$$

The amount of heat imparted or extracted during the isothermic process is equal to the work of expansion or compression in that process. Therefore, the heat taken from the source of work in the isothermic compression *a-0* is equal to that which is the equivalent of area *a-0-b-c*. Since $S_a = S_1 < S_0$, then the second member of the equation will have a plus sign.

---

* Excluding the final point *0* when pressures are equal.

** As we have said before, we are dealing with a source of work possessing the properties of an ideal gas.

Lastly, the last member of equation 5-40, $Ap_0(V_0-V_1)$, as can be seen from Fig. 5-26, will also have a plus sign and will be the equivalent of the area of figure *1-0-b-e*. Thus,

$$(L_w)_{max} = \text{area } 1\text{-}a\text{-}c\text{-}e + \text{area } 1\text{-}0\text{-}b\text{-}c - \text{area } a\text{-}0\text{-}b\text{-}c = \\ = \text{area } 1\text{-}a\text{-}0.$$

The shaded areas in Figs. 5-27 and 5-28 also show the value of the maximum useful work. In the first case (Fig. 5-27) the system is unbalanced in its initial state both thermically and mechanically since the temperature and the

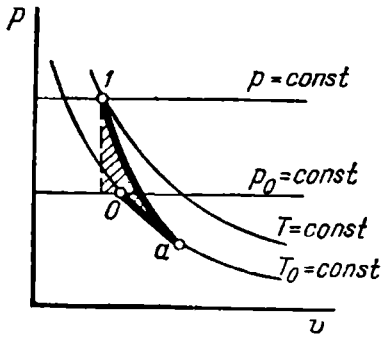


Fig. 5-27

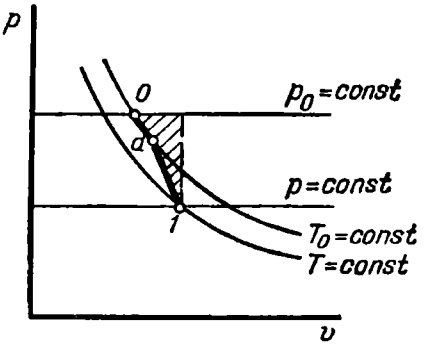


Fig. 5-28

pressure of the source of work are greater than T_0 and p_0. In the second case (Fig. 5-28) the system in its initial state is also unbalanced both thermically and mechanically, but here $T<T_0$ and $p<p_0$. We do not consider it necessary to explain how the maximum useful work is calculated in these two cases. The reader will easily be able to do it for himself on the basis of what has been said above.

Of still greater practical value than the maximum useful work of an isolated system is the maximum useful work of the heat. By this we understand the maximum useful work that can be performed by a working body that has passed through a full reversible cycle as a result of heat that has been imparted to it. In this case the system must be regarded as consisting of two heat reservoirs—one at a high and one at a low temperature—and a working body for which the reversible cycle is obligatory. As before, the surrounding medium is taken as the low-temperature reservoir and its practically unchanging parameters are T_0 and p_0. The high-temperature reservoir is often (but far from always)

taken as being infinitely great so that its temperature is also unchanging and is represented by T_1. Since the working body performs a cycle, as a result of which its internal energy remains unchanged, work can only be performed at the expense of heat imparted to it from the high-temperature reservoir. It is important to note that the ability of heat to perform work does not depend on the value of p_0, the pressure of the medium, because the volume of the working body remains unchanged after a cyclic process and the work does not result in either the compression or expansion of the medium; all the work performed by the working body during the cycle may be used for our own purposes, i. e., it is useful work.

In a cyclic process, the heat imparted to the working body by the high-temperature heat reservoir can only be partially converted into work during the cycle. A certain part of the heat must inevitably be transmitted to the low-temperature reservoir. The maximum work can be obtained when only reversible processes take place in the system and, consequently, when the entropy of the isolated system under examination remains unchanged.

The constancy of the total entropy of an isolated system in which reversible processes are taking place does not mean that the entropy of the individual bodies, or the sum of the bodies in the system, is also unchanged. The isolated system under discussion consists, as we have said, of two heat reservoirs and a working body. Since the working body is performing a cyclic process, all its parameters are unchanged at the end of the cycle irrespective of whether the processes taking place in the system are reversible or irreversible. The entropy of the low-temperature reservoir must necessarily increase because heat is imparted to it. The entropy of the high-temperature reservoir, however, will decrease since heat is taken from it. Since the total entropy of a closed system does not change when all the processes going on in the system are reversible, the increase in the entropy of the low-temperature reservoir ΔS_c must equal the decrease in the entropy of the high-temperature reservoir, ΔS_h, i. e.,

$$\Delta S_c = \Delta S_h; \tag{5-41}$$

this last equation is, as we have said, true only in cases when all the processes taking place in an isolated system are reversible.

After what has been said it will not be difficult to evolve the expression of the maximum useful work of the heat $(L'_\omega)_{max}$. Let Q_1 be the amount of heat imparted to the working body by the high-temperature heat reservoir. The amount of work performed during one cycle will be equal to the amount of heat obtained from the source minus the amount transmitted to the low-temperature reservoir. Since T_0, the temperature of the low-temperature reservoir, being that of the surrounding medium, remains practically unchanged, the amount of heat received by the medium, Q_0, may be represented by the product $T_0 \times \Delta S_c$.

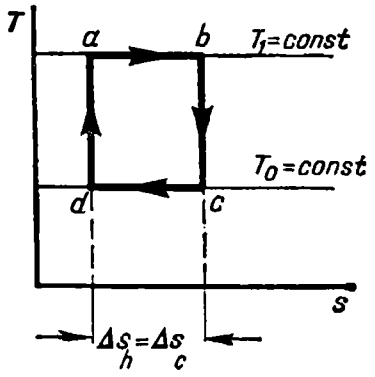


Fig. 5-29

Taking equation 5-41 into consideration we may write

$$Q_0 = T_0 \times \Delta S_h \qquad (5\text{-}42)$$

and

$$A\,(L'_\omega)_{max} = Q_1 - T_0 \times \Delta S_h. \qquad (5\text{-}43)$$

The Ts diagram in Fig. 5-29 shows the temperature of the hotter reservoir T_1 and that of the cooler reservoir (the medium) T_0. We know that the Carnot cycle will be the only possible reversible cycle when we are dealing with two heat reservoirs at constant temperatures. The essential condition for the Carnot cycle as represented by *abcd* (Fig. 5-29) to be reversible is that when heat is imparted to the working body its temperature must be the same as that of the hotter heat reservoir, and when heat is taken from the working body its temperature must be the same as that of the medium. In other words, the exchange of heat between the reservoirs and the working body must take place under conditions of an infinitely small difference in temperatures.

The Carnot cycle shown in Fig. 5-29 satisfies this requirement so that the absolute values of the entropy change in the two reservoirs are identical and the total change in the entropy of the isolated system is equal to zero.

The Ts diagram in Fig. 5-30 also shows the temperatures, T_1 and T_0, of the heat reservoirs and the Carnot cycle *abcd* performed by the working body. Since, however, the exchange of heat between the reservoirs and the working body takes place under conditions of a finite difference in temper-

atures ($T_1 > T'$ and $T'' > T_0$), the cycle is irreversible. The total change of the entropy of the isolated system, therefore, is not equal to zero.

It is very simple to prove this last condition. The high-temperature reservoir transfers to the working body an amount of heat which is equivalent to area *e-f-h-g*. All this heat is received by the working body when the latter is at a lower temperature, $T' < T_1$. The heat received by the working body is the equivalent of area *a-b-k-g*; obviously, area *e-f-h-g* = =area *a-b-k-g*. The working body then transfers to the low-temperature reservoir an amount of heat that is equivalent to area *d-c-k-g*. The low-temperature reservoir receives all this heat, but when it is at a lower temperature $T_0 < T''$. The heat received by the low-temperature source is the equivalent of area *l-m-n-g*; it is also obvious that area *d-c-k-g* = =area *l-m-n-g*.

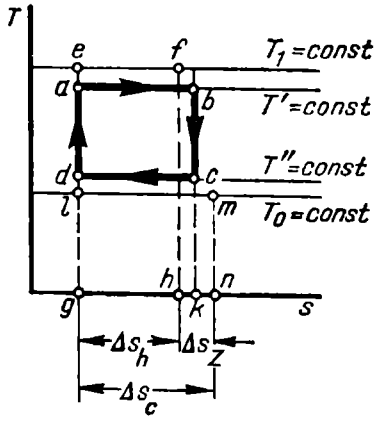


Fig. 5-30

Since the working body is performing a cyclic process, its entropy remains unchanged. Therefore, the total change of entropy in the isolated system is equal to the difference in the changes of entropy in the high- and low-temperature reservoirs, which, as can be seen from Fig. 5-30, will be a positive value:

$$\Delta S_z = \Delta S_c - \Delta S_h, \qquad (5\text{-}44)$$

where ΔS_z is the total change of entropy in the system.

A change of entropy in an isolated system only occurred because the processes in the system are irreversible; we may therefore say that

$$\Delta S_z = \Delta S_{ir}$$

where S_{ir} is the change of the entropy in an irreversible process.

Obviously the maximum useful work of the system, or the maximum useful work of the heat, will be the less, the greater the irreversibility of the processes, the measure of which is the increase of the entropy of the closed system

under discussion. Therefore, there must be a single relation between the reduction in the maximum possible useful work and the growth of entropy that is due to irreversibility. It will not be difficult for us to establish the nature of this relation.

Let there be an unbalanced closed system consisting of a source of work and a medium. Irrespective of whether the processes taking place in the system are reversible or irreversible, the internal energy of the source of work changes from the initial value U_1 to a value that is in equilibrium with the medium U_0.

This difference in the internal energy of the source of work (U_1-U_0) is partially converted into work and is partially transferred to the medium in the form of heat:

$$U_1-U_0=AL+Q_0. \tag{5-45}$$

The greater part of U_1-U_0 is converted into work if all the processes are reversible:

$$U_1-U_0=AL^{rv}+Q_0^{rv} \tag{5-46}$$

and, consequently,

$$L^{rv}=L_{max}.$$

In the case of irreversible processes

$$U_1-U_0=AL^{ir}+Q_0^{ir}. \tag{5-47}$$

By a comparison of equations 5-46 and 5-47 we get

$$AL^{rv}-AL^{ir}=\Delta AL=Q_0^{ir}-Q_0^{rv}; \tag{5-48}$$

ΔAL in the last equation represents the loss of useful work due to irreversibility. Since the temperature of the cooler reservoir, the medium, remains practically unchanged and is equal to T_0, we may write

$$Q_0^{rv}=T_0\times\Delta S^{rv}; \tag{5-49}$$

$$Q_0^{ir}=T_0\times\Delta S^{ir}. \tag{5-50}$$

From equations 5-48, 5-49 and 5-50 it follows that

$$\Delta AL+T_0(\Delta S^{ir}-\Delta S^{rv})$$

or,

$$\Delta AL=T_0\times\Delta S_{ir}. \tag{5-51}$$

In equation 5-51, $\Delta S_{ir}=\Delta S^{ir}-\Delta S^{rv}$ represents the increase in the entropy of an isolated system due to the irreversibility of the processes taking place in that system.

Equation 5-51 is of universal significance. If we are examining an isolated system consisting of two reservoirs of heat and a working body performing a cyclic process, the loss of ability to perform work may be expressed by the same equation 5-51. In this case we have

$$AL'_w = Q_1 - Q_0 = Q_1 - T_0 \times \Delta S_c; \qquad (5\text{-}52)$$

as the reader will remember, Q_1 in this equation is the amount of heat imparted to the working body by the hotter reservoir and Q_0 the amount of heat transmitted by the working body to the cooler reservoir. But, according to equation 5-43, in cases of reversibility

$$A\,(L'_w)_{max} = Q_1 - T_0 \times \Delta S_h.$$

Therefore,

$$\Delta AL = A\,(L'_w)_{max} - AL'_w = T_0\,(\Delta S_c - \Delta S_h),$$

but the difference, $\Delta S_c - \Delta S_h$, is precisely the increase in the entropy of the isolated system due to irreversibility, ΔS_{ir}, so that

$$\Delta AL = T_0 \times \Delta S_{ir},$$

i. e., we have again, as should have been expected, obtained equation 5-51.

Equation 5-51 is a convenient means of analysing the economical working of heat installations. This is usually called the entropy computation of energy losses and has become widespread in its use in recent years.

As far as the determination of the value of ΔS_{ir} is concerned, no recommendations of a general character can be given in this course. The determination of ΔS_{ir} is not always a simple problem and must be carried out separately for every actual process.

Chapter Six

THE DIFFERENTIAL EQUATIONS OF THERMODYNAMICS

6-1. The Heat, Internal Energy, Enthalpy and Entropy Equations. Of those thermodynamic parameters known to us only p, v and t may be obtained directly by experiment. The equations of the first and second laws of thermodynamics, however, enable us to establish a number of analytical relations between the parameters of any body in differential form. Owing to the existence of these relations between parameters that can be established by measurement, the remainder can be obtained by integrating the corresponding differential equations, the compilation of which is the subject of this chapter.

According to the first law of thermodynamics for reversible processes

$$dq = du + Ap\,dv, \tag{6-1}$$

or, in another version (equation 3-36)

$$dq = di - Av\,dp. \tag{6-2}$$

According to the second law

$$dq = T\,ds. \tag{6-3}$$

Combining equations 6-1 and 6-3, we get

$$T\,ds = du + Ap\,dv. \tag{6-4}$$

The basic parameters are, as we have said, p, v and T; but of these only two are independent for homogeneous bodies such as gases and superheated vapours. Therefore, any two of them, p and T, v and T, p and v determine all other parameters.

Taking v and T as the independent variables, we may get relations of a general type:

$$p = f_1(v,T);$$
$$u = f_2(v,T);$$
$$i = f_3(v,T);$$
$$s = f_4(v,T).$$

Equations 6-1, 6-2 and 6-3 contain the value q which, it will be remembered, is not a function of state and is, therefore, not a value describing the state. It is expedient to express it by heat capacity according to the relation

$$dq = c\,dT.$$

Therefore, according to equation 6-1

$$c\,dT = du + Ap\,dv$$

and, when $v = \text{const}$

$$c_v\,dT_v = du_v,$$

whence

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v. \tag{6-5}$$

According to equation 6-3, when $v = \text{const}$

$$c_v dT_v = T ds_v$$

and, therefore,

$$c_v = T\left(\frac{\partial s}{\partial T}\right)_v. \tag{6-6}$$

When $p = \text{const}$, by equation 6-2 we get

$$c_p dT_p = di_p$$

and, therefore,

$$c_p = \left(\frac{\partial i}{\partial T}\right)_p, \tag{6-7}$$

and by equation 6-3, when $p = \text{const}$

$$c_p dT_p = T ds_p$$

and, therefore,

$$c_p = T\left(\frac{\partial s}{\partial T}\right)_p. \tag{6-8}$$

To begin with, let us assume that the independent variables are v and T.

From equation 6-4

$$ds = \frac{du}{T} + \frac{Ap\,dv}{T},$$

and, by the rules of the differential calculus, since $u = f_2(v, T)$,

$$du = \left(\frac{\partial u}{\partial v}\right)_T dv + \left(\frac{\partial u}{\partial T}\right)_v dT$$

and, therefore,

$$ds = \left(\frac{\partial u}{\partial v}\right)_T \frac{\partial v}{T} + \left(\frac{\partial u}{\partial T}\right)_v \frac{\partial T}{T} + \frac{Ap\,dv}{T},$$

or

$$ds = \frac{1}{T}\left(\frac{\partial u}{\partial T}\right)_v dT + \frac{1}{T}\left[\left(\frac{\partial u}{\partial v}\right)_T + Ap\right] dv.$$

But, since $s = f_4(v, T)$, we may also write

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv.$$

Comparing this equation with the previous one, we conclude that

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{1}{T}\left(\frac{\partial u}{\partial T}\right)_v; \tag{6-9}$$

$$\left(\frac{\partial s}{\partial v}\right)_T = \frac{1}{T}\left[\left(\frac{\partial u}{\partial v}\right)_T + Ap\right]. \tag{6-10}$$

Taking the partial derivative of equation 6-9 for v (with T constant), we get:

$$\frac{\partial^2 s}{\partial T\,\partial v} = \frac{1}{T}\frac{\partial^2 u}{\partial T\,\partial v}.$$

Then, let us take the partial derivative of equation 6-10 for T (with v constant):

$$\frac{\partial^2 s}{\partial v\,\partial T} = \frac{1}{T}\left[\frac{\partial^2 u}{\partial v\,\partial T} + A\left(\frac{\partial p}{\partial T}\right)_v\right] - \frac{1}{T^2}\left[\left(\frac{\partial u}{\partial v}\right)_T + Ap\right].$$

These derivatives are obviously equal, i. e.,

$$\frac{1}{T}\frac{\partial^2 u}{\partial T\,\partial v} = \frac{1}{T}\left[\frac{\partial^2 u}{\partial v\,\partial T} + A\left(\frac{\partial p}{\partial T}\right)_v\right] - \frac{1}{T^2}\left[\left(\frac{\partial u}{\partial v}\right)_T + Ap\right],$$

whence

$$A\left(\frac{\partial p}{\partial T}\right)_v = \frac{1}{T}\left[\left(\frac{\partial u}{\partial v}\right)_T + Ap\right]$$

and, therefore,

$$\left(\frac{\partial u}{\partial v}\right)_T = AT\left(\frac{\partial p}{\partial T}\right)_v - Ap. \qquad (6\text{-}11)$$

Substituting this value in equation 6-10, we get

$$\left(\frac{\partial s}{\partial v}\right)_T = A\left(\frac{\partial p}{\partial T}\right)_v. \qquad (6\text{-}12)$$

Equations 6-11 and 6-12 give us the change in the internal energy and the entropy as functions of the variables p, v and T in an isothermic process. We may also use them to obtain the full differentials du and ds, i. e., the changes in u and s are dependent on p, v, and T in any process.

We have already had

$$du = \left(\frac{\partial u}{\partial v}\right)_T dv + \left(\frac{\partial u}{\partial T}\right)_v dT;$$

taking $\left(\frac{\partial u}{\partial v}\right)_T$ from equation 6-11 and $\left(\frac{\partial u}{\partial T}\right)_v = c_v$ from equation 6-5 and substituting in the last equation, we get

$$du = \left[AT\left(\frac{\partial p}{\partial T}\right)_v - Ap\right] dv + c_v dT. \qquad (6\text{-}13)$$

Similarly

$$ds = \left(\frac{\partial s}{\partial v}\right)_T dv + \left(\frac{\partial s}{\partial T}\right)_v dT;$$

taking $\left(\frac{\partial s}{\partial v}\right)_T$ from equation 6-12 and $\left(\frac{\partial s}{\partial T}\right)_v = \frac{c_v}{T}$ from equation 6-6 and substituting in this equation, we get

$$ds = A\left(\frac{\partial p}{\partial T}\right)_v dv + \frac{c_v}{T} dT. \qquad (6\text{-}14)$$

Furthermore, by equation 6-3

$$dq = Tds,$$

i. e.,

$$dq = AT\left(\frac{\partial p}{\partial T}\right)_v dv + c_v dT. \qquad (6\text{-}15)$$

Therefore, if we have the equations of state which interconnect the parameters p, v and T, we can apply equations 6-13, 6-14 and 6-15 to determine the changes in internal energy and entropy and also the amount of heat imparted

or extracted in any process as long as c_v is known. But the value of c_v is also determined by an equation of state as we shall later establish.

For ideal gases

$$pv = RT$$

and, therefore,

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v};$$

by substituting this in equation 6-13, we get

$$du = \left(\frac{ART}{v} - Ap\right) dv + c_v dT =$$

$$= \left(\frac{Apv}{v} - Ap\right) dv + c_v dT = c_v dT,$$

as we have already established.

According to equation 6-11

$$\left(\frac{\partial u}{\partial v}\right)_T = 0,$$

i. e., the internal energy of an ideal gas does not change when the volume is changed isothermically; in other words, its internal energy is not dependent on volume and is a function of temperature alone. From this it follows that c_v, too, can be a function only of temperature.

Let us now assume that p and T are the independent variables. Comparing equations 6-2 and 6-3 we get

$$T\,ds = di - Av\,dp,$$

whence,

$$ds = \frac{di}{T} - \frac{Av}{T}\,dp.$$

But, since $i = f_3'(p, T)$,

$$di = \left(\frac{\partial i}{\partial p}\right)_T dp + \left(\frac{\partial i}{\partial T}\right)_p dT,$$

so that

$$ds = \left(\frac{\partial i}{\partial T}\right)_p \frac{dT}{T} + \frac{1}{T}\left[\left(\frac{\partial i}{\partial p}\right)_T - Av\right] dp.$$

On the other hand, since $s = f_4'(p, T)$

$$ds = \left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial p}\right)_T dp.$$

Comparing this equation with the previous one, we conclude

$$\left(\frac{\partial s}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial i}{\partial T}\right)_p; \tag{6-16}$$

$$\left(\frac{\partial s}{\partial p}\right)_T = \frac{1}{T}\left[\left(\frac{\partial i}{\partial p}\right)_T - Av\right]. \tag{6-17}$$

Let us take the partial derivative of equation 6-16 for p (with T constant) and the partial derivative of equation 6-17 for T (with p constant); we get

$$\frac{\partial^2 s}{\partial T\,\partial p} = \frac{1}{T}\frac{\partial^2 i}{\partial T\,\partial p};$$

$$\frac{\partial^2 s}{\partial p\,\partial T} = \frac{1}{T}\left[\frac{\partial^2 i}{\partial p\,\partial T}\left(-A\frac{\partial v}{\partial T}\right)_p\right] - \frac{1}{T^2}\left[\left(\frac{\partial i}{\partial p}\right)_T - Av\right].$$

These derivatives are obviously equal, i. e.,

$$\frac{1}{T}\frac{\partial^2 i}{\partial T\,\partial p} = \frac{1}{T}\left[\frac{\partial^2 i}{\partial p\,\partial T} - A\left(\frac{\partial v}{\partial T}\right)_p\right] - \frac{1}{T^2}\left[\left(\frac{\partial i}{\partial p}\right)_T - Av\right],$$

or

$$A\left(\frac{\partial v}{\partial T}\right)_p = -\frac{1}{T}\left[\left(\frac{\partial i}{\partial p}\right)_T - Av\right],$$

whence

$$\left(\frac{\partial i}{\partial p}\right)_T = -AT\left(\frac{\partial v}{\partial T}\right)_p + Av. \tag{6-18}$$

Substituting this value in equation 6-17, we get

$$\left(\frac{\partial s}{\partial p}\right)_T = -A\left(\frac{\partial v}{\partial T}\right)_p. \tag{6-19}$$

Equations 6-18 and 6-19 give the change in i and s for an isothermic process, but by applying them we can get the changes di and ds for any process.

We have already had

$$di = \left(\frac{\partial i}{\partial p}\right)_T dp + \left(\frac{\partial i}{\partial T}\right)_p dT;$$

substituting in this equation $\left(\frac{\partial i}{\partial p}\right)_T$ from equation 6-18 and $\left(\frac{\partial i}{\partial T}\right)_p = c_p$ from equation 6-7, we get

$$di = c_p dT - A\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right] dp. \tag{6-20}$$

Similarly,

$$ds = \left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial p}\right)_T dp;$$

and substituting in this equation $\left(\frac{\partial s}{\partial T}\right)_T = \frac{c_p}{T}$ from equation 6-8 and $\left(\frac{\partial s}{\partial p}\right)_T$ from equation 6-19, we get

$$ds = \frac{c_p}{T} dT - A \left(\frac{\partial v}{\partial T}\right)_p dp. \qquad (6\text{-}21)$$

Furthermore, by equation 6-3, $dq = T\,ds$, i. e.,

$$dq = c_p dT - AT \left(\frac{\partial s}{\partial T}\right)_p dp. \qquad (6\text{-}22)$$

For ideal gases

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p}$$

and, therefore, by equation 6-20

$$di = c_p dT - A\left(\frac{RT}{p} - v\right) dp = c_p dT,$$

and by equation 6-18

$$\left(\frac{\partial i}{\partial p}\right)_T = 0,$$

i. e., the enthalpy of an ideal gas does not change with an isothermic change of state; in other words, its enthalpy does not depend on pressure but is a function of the temperature alone. From this it follows that c_p can be a function only of the temperature.

In an exactly similar manner the corresponding differential equations can be obtained in which p and v are taken as the dependent variables.

6-2. The Equations of Heat Capacities c_p and c_v. In the most general case, according to equation 6-15,

$$dq = AT \left(\frac{\partial p}{\partial T}\right)_v dv + c_v dT;$$

when $p = \text{const}$, $dq = c_p dT_p$, so that

$$c_p dT_p = AT \left(\frac{\partial p}{\partial T}\right)_v dv_p + c_v dT_p,$$

whence,

$$c_p - c_v = AT\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p. \qquad (6\text{-}23)$$

For ideal gases

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v} \text{ and } \left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p},$$

which after substitution yields

$$c_p - c_v = AT\frac{R}{v} \times \frac{R}{p} = AR.$$

According to equation 6-8

$$\left(\frac{\partial s}{\partial T}\right)_p = \frac{c_p}{T};$$

let us take the partial derivative of this equation for p (T being constant); we get

$$\frac{\partial^2 s}{\partial T\, \partial p} = \frac{1}{T}\left(\frac{\partial c_p}{\partial p}\right)_T.$$

According to equation 6-19

$$\left(\frac{\partial s}{\partial p}\right)_T = -A\left(\frac{\partial v}{\partial T}\right)_p;$$

let us take the partial derivative of this equation for T (p being constant); we get

$$\frac{\partial^2 s}{\partial p\, \partial T} = -A\left(\frac{\partial^2 v}{\partial T^2}\right)_p.$$

These partial derivatives are equal, i. e.,

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -AT\left(\frac{\partial^2 v}{\partial T^2}\right)_p. \qquad (6\text{-}24)$$

This equation shows us the dependence of c_p on pressure.

If the dependence of the heat capacity c_p on the pressure and temperature has been found experimentally, we may discover the relation between p, v and T, i. e., the equation of state, by doubly integrating equation 6-24.

In exactly the same way the equation for c_v is evolved. According to equation 6-6,

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{c_v}{T};$$

let us take the partial derivative of this equation for v (T being constant); we get

$$\frac{\partial^2 s}{\partial T\, \partial v} = \frac{1}{T}\left(\frac{\partial c_v}{\partial v}\right)_T.$$

According to equation 6-12,

$$\left(\frac{\partial s}{\partial v}\right)_T = A\left(\frac{\partial p}{\partial T}\right)_v;$$

let us take the partial derivative of this equation for T (v being constant); we get

$$\frac{\partial^2 s}{\partial v\, \partial T} = A\left(\frac{\partial^2 p}{\partial T^2}\right)_v;$$

and, since these derivatives are equal

$$\left(\frac{\partial c_v}{\partial v}\right)_T = AT\left(\frac{\partial^2 p}{\partial T^2}\right)_v. \qquad (6\text{-}25)$$

This equation shows how c_v depends on the volume.

For ideal gases

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v} \text{ and } \left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0,$$

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} \text{ and } \left(\frac{\partial^2 v}{\partial T^2}\right)_p = 0,$$

so that equations 6-24 and 6-25 become

$$\left(\frac{\partial c_p}{\partial p}\right)_T = 0 \text{ and } \left(\frac{\partial c_v}{\partial v}\right)_T = 0,$$

i. e., the heat capacities c_p and c_v of ideal gases do not depend on pressure and volume and can be functions of the temperature alone.

Chapter Seven

THE CYCLES OF INTERNAL COMBUSTION PISTON ENGINES

7-1. The Principle of the Internal Combustion Engine. The thermal efficiency (η_t) of a cycle is, in general, the greater, the higher the maximum and lower the minimum temperatures of the working body. The heat to be converted into work in heat engines is obtained by igniting a fluid or gaseous fuel, the combustion of which develops relatively high temperatures. It is clear that if we wish to make use of the high temperature created by combustion we must burn the fuel inside the engine itself and use the gaseous products of combustion, the vehicle of this high temperature, as the working body. The engines in which this is done are called *internal combustion engines*. In these engines the highest temperature is that of combustion and this gives them the advantage of very high thermal efficiency, η_t.

An internal combustion engine, since it employs the gaseous products of combustion as a working body, is, in the broadest sense of the word, a *gas engine*. In principle, any fuel may be used in it—solid, liquid or gaseous—but in modern practice only liquid and gaseous fuels are used. The most widely used gaseous fuels are generator and blast-furnace gases; an engine working on such a fuel is a *gas engine* in the narrow sense of the word.

Generator gas is obtained by the incomplete combustion of solid fuel in a *generator*. The carbon of the fuel produces, on combustion, carbon monoxide (CO) and the moisture contained in the fuel, or water vapour specially introduced into the gas generator, disintegrates into hydrogen and oxygen; the latter combines with the carbon of the fuel and produces an additional quantity of carbon monoxide. The process of generation produces a gas which has as its chief combustible elements carbon monoxide and hydrogen, with

a small admixture of methane (CH_4). The composition of the gas is largely dependent on the type of fuel used—coke, anthracite, bituminous and brown coal, wood and peat. Thus, the solid fuel is used for the generator and the generator gas is introduced into the engine.

Blast-furnace gas is a by-product, or rather a waste product, of iron smelting; this furnace gas approximates generator gas in composition.

In engines that employ gas fuels the gas is mixed with a certain amount of air and the mixture is introduced into the engine where it is ignited by an electric spark. Combustion provides an increased amount of heat, the products of combustion expand and perform work.

Liquid fuels—petrol, spirit, kerosene, crude oil—are introduced into the engine in an atomised state together with the necessary amount of air and form the fuel mixture. Such engines are called petrol, spirit, kerosene or oil engines according to the fuel they use.

The direct use of solid fuel in internal combustion engines by introducing it into the engine in powder form is of great practical interest because solid fuel is considerably cheaper than liquid fuel and the generating process to produce gas from solid fuel involves the loss of 20%-25% of the heat in the generator itself. Experiments in this field have been conducted for a long time but so far no satisfactory results have been achieved; the chief difficulties are mixing the fuel with air and removing the ash from the engine.

In present-day practice, in addition to internal combustion piston engines, gas turbines or internal combustion turbines, are widely used.

7-2. The Cyclic Process in an Internal Combustion Engine. Actually internal combustion engines do not employ cyclic processes because the gaseous products of combustion, having expanded and transferred the work to the crankshaft, are expelled from the engine and their place is taken by a fresh portion of the fuel mixture which greatly changes its composition as a result of the subsequent process of combustion. Changes in the chemical composition of the working body are effected in one direction only, i. e., the fuel mixture is transformed into the products of combustion; the return of the products of combustion to their original state is impossible in practice. Nevertheless we may speak con-

ditionally of the cycle of an internal combustion engine if we ignore the chemical changes and determine its efficiency $\eta_t = \frac{Al}{q_1}$, employing values for the work, l, and the expenditure of heat, q_1, that are theoretically those of the engine. The inaccuracy involved in this is relatively small because the gas constant of the fuel mixture and the products of combustion differ but little from each other despite the radical chemical changes resulting from combustion.

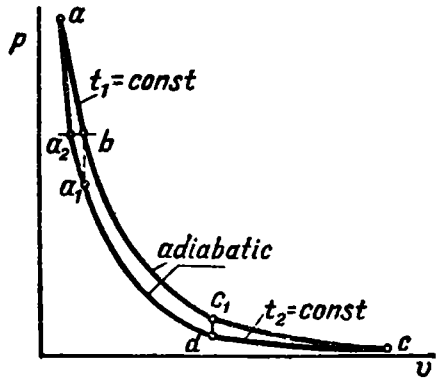


Fig. 7-1

From the theoretical standpoint it is desirable to apply the Carnot cycle in an internal combustion engine as in any other heat engine but in reality this is impractical for the following reasons. As a result of the insignificant difference in the slope of the isotherms and adiabatics of the gases despite a very great difference in the temperatures t_1 and t_2, the pv diagram of the internal combustion engine cycle is greatly extended both in the vertical and horizontal directions, i. e., the cycle involves great pressures and volumes, as we can see from the following.

By equation 5-6 the work of the Carnot cycle *abcd* (Fig. 7-1)

$$l = R(T_1 - T_2) \ln \delta,$$

where $\delta = \frac{v_b}{v_a} = \frac{p_a}{p_b}$ — the isothermic expansion ratio, and since the adiabatic *bc* according to equation 4-30 is

$$\frac{T_2}{T_1} = \left(\frac{p_c}{p_b}\right)^{\frac{k-1}{k}} \quad \text{and} \quad p_b = p_c \left(\frac{T_1}{T_2}\right)^{\frac{k}{k-1}},$$

then

$$\delta = \frac{p_a}{p_b} = \frac{p_a}{p_c}\left(\frac{T_2}{T_1}\right)^{\frac{k}{k-1}}$$

and, consequently,

$$l = R(T_1 - T_2) \ln \left[\frac{p_a}{p_c}\left(\frac{T_2}{T_1}\right)^{\frac{k}{k-1}}\right].$$

It follows from this last equation that the work l is positive only when the logarithmic expression in square brackets is greater than unity, i. e., when

$$\frac{p_a}{p_c} > \left(\frac{T_1}{T_2}\right)^{\frac{k}{k-1}}.$$

The practical values employed in modern engines are $t_1 = 1800°$ C, $t_2 = 15°$ C and $p_c = 1$ ata when $k = 1.33$; substituting these values we get $p_a > 2{,}880$ ata, i. e., under the given conditions the Carnot cycle involves pressures in the 3,000 ata range which are absolutely fantastic compared with those used in modern engines which rarely exceed 100 ata.

On the other hand we have

$$p_a v_a = RT_1 \text{ and } p_c v_c = RT_2$$

and, therefore

$$\frac{v_c}{v_a} = \frac{p_a}{p_c} \times \frac{T_2}{T_1}.$$

If $p_a = 2{,}880$ ata

$$\frac{v_c}{v_a} = \frac{2{,}880}{1} \times \frac{288}{2{,}073} = 400,$$

i. e., under the conditions given in our example the working body expands inside the engine more than 400 times; in real engines the expansion does not usually exceed 16 times. An expansion ratio in the vicinity of 400 would involve very clumsy cylinders that are not relevant to the power of the engine, would make the engine more expensive and decrease the amount of heat actually used on account of the great losses from friction.

By rejecting the isothermic processes ab and cd and substituting for them the isochoric processes a_1b and c_1d, or the isobaric process a_2b and the isochoric c_1d, we get the cycles a_1bc_1d and a_2bc_1d within the limits of temperatures t_1 and t_2 but with a lowered maximum pressure and a lesser expansion ratio. The thermal efficiency of these cycles is naturally lower than that of the Carnot cycle, $\eta_{t_0} = 1 - \frac{T_2}{T_1}$; but the actual use of the heat is greater on account of smaller friction losses.

The cycles a_1bc_1d and a_2bc_1d actually differ from one another only in the processes a_1b and a_2b during which heat is imparted to the body by the processes of combustion; in the first cycle the combustion takes place with a constant volume

and in the second with a constant pressure. Both cycles are carried out approximately in modern internal combustion piston engines.

7-3. The Constant-Volume Combustion Cycle. The investigation of the work of a piston engine is best accomplished by the use of the *pV* graph in which the abscissae show the volumes occupied by the working body in the cylinder, and the ordinates give the corresponding absolute pressures. Since the changes in the volume of the working body in the cylinder are directly proportional to the shifting of the piston, this graph must show the changes in pressure in the cylinder depending on the shifting of the piston. These diagrams for piston engines are known as *indicator diagrams* because they are compiled for engines at work with the aid of an indicator that produces the closed curve of the pressure changes in the cylinder depending on the position of the piston; the indicators are actually self-recording manometers. The area of the figure in the indicator diagram gives the value of the *indicated work* of one cycle inside the cylinder, drawn to a definite scale.

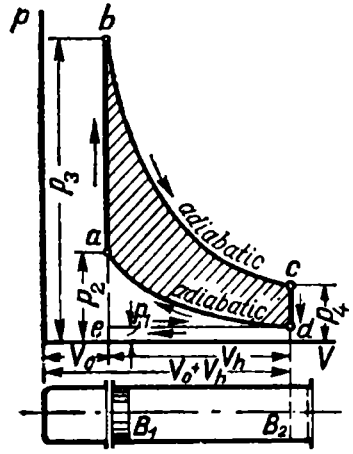


Fig. 7-2

This indicator diagram must not be confused with the *pv* diagram of the cycle which shows the changes in the working body, or, more exactly, the changes in pressure and specific volume; the indicator diagram shows the changes in pressure inside the cylinder that depend on the position of the piston and, as we shall see later, not all the curves in the indicator diagram show changes in the state of the body.

The theoretical indicator diagram of an engine employing combustion at constant volume is given in Fig. 7-2 and below it there is a schematic longitudinal cross-section of the cylinder. The piston, in moving from one position of rest (left dead centre: LDC) at point B_1 to the other position of rest (right dead centre: RDC) at point B_2, sucks a mixture of fuel and air into the left-hand part of the cylin-

der through a valve in the cylinder head (not shown in the diagram) at a constant pressure of p_1 (equal to the pressure of the outside air, i. e., the atmosphere); this is the *suction stroke* that in our diagram is represented by the horizontal line *ed*; theoretically the state of the gas does not change throughout the length of line *ed*, the only change being in the weight and volume of the gas in the cylinder; the line *ed* is not, therefore, a line indicating change of state. When the piston reaches RDC at point B_2, the inlet valve closes and the piston, moving to the left, compresses the gas in the cylinder according to adiabatic curve *da*, the pressure increasing from p_1 at RDC to p_2 at LDC. This is the *compression stroke*; the adiabatic curve *da* indicates a change in the state of the gas because it refers to the same weight of the mixture in the cylinder throughout its entire length. When the piston is at position B_1, LDC, the mixture in the cylinder is ignited by an electric spark and combustion takes place, theoretically at constant volume, i. e., instantaneously, thus producing heat. Owing to this combustion, which has the character of an explosion, the pressure in the cylinder increases from p_2 to p_3 along the vertical *ab* which, like the adiabatic *da*, is a line showing a change in the state of the working body. The specific feature of the process *ab* is that not only the pressure and the temperature but also the chemical composition of the body change; at point *a* there is a fuel mixture and at point *b* there are the products of combustion.

The explosion forces the piston to the right and the products of combustion expand to the end of the stroke along adiabatic *bc*, and their pressure simultaneously drops from p_3 to p_4. This is the *ignition stroke* (power stroke) and the adiabatic *bc* shows the change in the state of the products of combustion. When the piston reaches RDC, a valve in the piston-head (not shown in the diagram) opens, connecting the interior of the cylinder with the outside atmosphere and theoretically the pressure in the cylinder instantaneously drops from p_4 to the outside pressure p_1 which is shown in the diagram by the vertical line *cd*, and part of the products of combustion flies out of the cylinder with a more or less loud noise (exhaust). The vertical, *cd*, is not a line indicating a change of state; in actual fact the reduction in the pressure of the products of combustion from p_4 to p_1 as the valve opens is not due to the extraction of heat as by

the isochor *cd*, but exclusively to the equalising of the pressure in the cylinder with that of the external medium which, theoretically speaking, takes place instantaneously without an exchange of heat and must, therefore, be adiabatic. At the time of the drop in pressure shown by the vertical line *cd* in the indicator diagram, the products of combustion expand adiabatically from pressure p_4 to pressure p_1 and, as there is no room for them in the cylinder, they fly out. For this reason the change in the state of the products of combustion *cd* at the time the exhaust valve opens is depicted by the section of the adiabatic cc_1 (Fig. 7-3) which is the continuation of the adiabatic *bc* beyond point *c* to the point c_1 where it meets the isobar of external pressure, p_1. Expansion *bc* takes place in the cylinder and expansion cc_1 in the exhaust pipe; the section of the curve $dc_1=V_{c1}-V_c$ gives the volume of the exhaust gases that leave the cylinder, and point c_1 determines the state of the products of combustion corresponding to point *d* on the exhaust line *cd* of the indicator diagram.

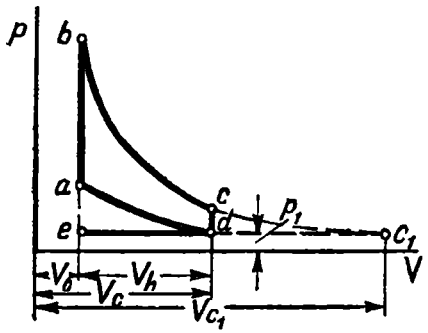


Fig. 7-3

When the exhaust valve opens, the piston, moving to the left, ejects the products of combustion at constant pressure p_1, their volume, V_h, being equal to the *volume of the cylinder* (the product of the interior cross-section area and the length of the piston stroke). This is the *exhaust stroke* (the horizontal line *de* in the indicator diagram) during which, theoretically, the state of the products of combustion remains unchanged, the only change being in the weight and volume of the gas left in the cylinder; line *de*, therefore, does not indicate a change of state. When the piston reaches LDC, the exhaust valve closes and the inlet valve opens, permitting a fresh portion of the fuel mixture to enter the cylinder; this fresh portion is sucked in by the piston as it moves to the right and mixes with the exhaust gases remaining in the cylinder; these products of combustion left over from the previous cycle have a volume of V_0, which is the volume of the *combustion chamber*; thus we obtain a fresh fuel mixture

for a repetition of the compression *da* and combustion *ab*, i. e., for the next cycle. This is the fuel mixture without which the processes of compression *da* and combustion *ab* could not take place.

In the given engine, the full working process, by means of which work (represented by the shaded area *abcd* in Fig. 7-2) is obtained from the combustion of a definite amount of fuel, is completed in four strokes, or two revolutions of the crankshaft; it is, therefore, called a four-stroke engine.

Thus when the fuel mixture enters the engine, its state is that shown by point *d* (Fig. 7-3); it undergoes changes of state *da*, *ab* and bc_1 and is then ejected from the cylinder in the form of products of combustion whose state is c_1; a further portion of the fuel mixture is then introduced into the engine. Since the products of combustion are not transferred to the next process, there is a break between points c_1 and *d*, that is, there is no cyclic process. Nevertheless the cycle may be completed by isobar c_1d since the products of combustion are cooled in the air at constant pressure p_1 until they reach the outside temperature, i. e., until they reach the initial temperature of the mixture at point *d*. This would be fully permissible if the gas constant of the fuel mixture and that of the products of combustion were identical; it is also permissible in practice because, as we have said, there is a very small difference in the gas constants. It is simpler and more advantageous, however, to complete the cycle with the isochor *cd*, and not with the isobar c_1d, and to study the cycle *abcd*. In the cycles *abcd* and abc_1d the amount of heat imparted to the working body will be the same because they have a common combustion process *ab*; the work of the cycle, however, differs. In cycle *abcd* it is equal to the theoretical work of the engine, measured as area *abcd*; in cycle abc_1d it is greater by area cc_1d, the amount lost in practice because the work of expansion cc_1 is not transmitted to the piston. And since this loss is inevitable in the engine under discussion even theoretically it is better to calculate the thermal efficiency, η_t, of the cycle *abcd*.

Thus, we accept the premise that the cycle of this engine consists of two isochors and two adiabatics. In Figs. 7-4 and 7-5 the cycle is shown in parallel *pv* and *Ts* diagrams. We shall compute its efficiency, assuming for the sake of

simplicity that c_p and c_v and, consequently, $k = \frac{c_p}{c_v}$ and R are constant for the whole cycle.

Heat is imparted to the working body only during the combustion process *ab*, its quantity being

$$q_1 = c_v (T_3 - T_2)$$

which is area $ABB'A'$ in Fig. 7-5, and is taken away only during process *cd*, the quantity being

$$q_2 = c_v (T_4 - T_1)$$

which is area $DCB'A'$.

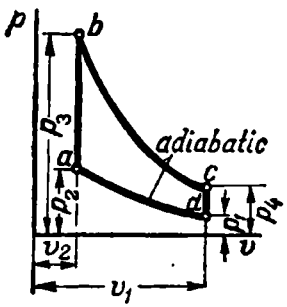


Fig. 7-4

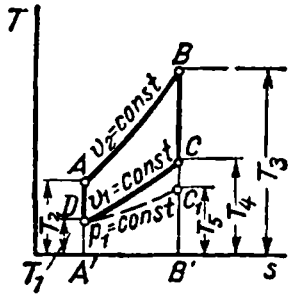


Fig. 7-5

By equation 5-8, therefore

$$\eta_t = 1 - \frac{q_2}{q_1} = 1 - \frac{c_v (T_4 - T_1)}{c_v (T_3 - T_2)} = 1 - \frac{T_4 - T_1}{T_3 - T_2} = 1 - \frac{T_1}{T_2} \times \frac{\frac{T_4}{T_1} - 1}{\frac{T_3}{T_2} - 1}.$$

On the other hand, by equation 4-30, for the adiabatic *da* we have

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{k-1} = \varepsilon^{k-1}$$

and similarly for adiabatic *bc*

$$\frac{T_3}{T_4} = \left(\frac{v_1}{v_2}\right)^{k-1} = \varepsilon^{k-1}$$

where ε is the adiabatic compression or expansion ratio, identical for the given process; therefore,

$$\frac{T_2}{T_1} = \frac{T_3}{T_4} \text{ or } \frac{T_4}{T_1} = \frac{T_3}{T_2}.$$

Making the necessary substitutions in the efficiency expression we get

$$\eta_t = 1 - \frac{1}{\varepsilon^{k-1}}. \qquad (7\text{-}1)$$

The simplification we have undertaken gives us a very simple expression for η_t; it may be used for practical calculations, k being taken as 1.33.

As we see from equation 7-1, the thermal efficiency of the cycle is fully determined by the adiabatic compression or expansion ratio (ε) and increases as the latter increases; this is quite understandable because by increasing ε we increase v_1 or decrease v_2, i. e., we lower isochor CD or raise isochor AB, in other words, we either reduce q_2 or increase q_1 and thereby increase the efficiency η_t. An increase of ε means an increase in the difference in temperatures $(T_3 - T_1)$, that is, by increasing the drop in temperature in a cyclic process we thereby increase its efficiency, η_t.

By equation 7-1, for various degrees of compression at $k = 1.33$, we get

$\varepsilon =$	4	5	6	7	8	9
$\eta_t =$	36.7	41.2	44.6	47.4	49.6	51.5 %.

The development and perfection of internal combustion engines has always been connected with the problem of increasing the compression ratio; in the early eighties of the last century, pressure at the end of the compression stroke was no more than 2-2.5 ata, whereas today it reaches 12 ata and more with certain generator and blast-furnace gases. The composition of the combustible mixture, however, determines the limit to which ε may be increased because an increase in adiabatic compression gives a simultaneous rise in temperature from T_1 to T_2 which must always be below the temperature of spontaneous combustion in order to prevent the explosion occurring spontaneously before the piston reaches the end position; such premature ignition is not only detrimental to the work of the engine from the standpoint of heat conversion but may lead to breakages or to the engine coming to a standstill. At first sight it might seem that it would be sufficient to limit the degree of compression to obtain the temperature of spontaneous combustion at the end of the stroke; the mixture would explode spontaneously

and no artificial ignition would be required. This is impermissible in practice because the change in temperature during compression varies as the load on the engine, and on account of cooling conditions and a number of other factors; an engine calculated for spontaneous combustion at the moment the piston is motionless may produce premature ignition or no ignition at all.

The poorer a mixture, i. e., the fewer the combustible particles it contains, the higher the temperature of spontaneous combustion and the greater the permissible compression ratio. There is, however, a limit to the rarefication of the mixture with air because very poor mixtures are difficult to ignite and may not burn at all.

Thus, we come to the conclusion that it is desirable, for the engine under discussion, to work with small doses of fuel mixed with air since this enables us to employ high pressures and increase efficiency.

All gas engines as well as petrol, spirit and kerosene engines work according to this cycle.

In conclusion it must be said that the isochor CD is an imaginary process; in actual fact the change of state in the products of combustion between points C and D takes place according to adiabatic CC_1 and isobar C_1D; point C_1, where adiabatic BC intersects isobar p_1, determines the temperature T_5 of the products of combustion that are ejected from the cylinder by the piston. Area DCC_1 gives the loss from the incomplete expansion of the gases in the cylinder; it increases the waste heat q_2*.

7-4. The Constant-Pressure Combustion Cycle. The constant effort to design internal combustion engines to work more economically has led, as we said above, to higher compression ratios. In the engine we examined the limit is provided by the temperature of spontaneous combustion, on account of which ε is rarely more than eight. This limiting factor is removed if the fuel and the air are compressed separately. Separate compression is convenient in practice because the fuel, injected into a working chamber containing com-

* It must be remembered that the process CC_1 is a typical irreversible process (adiabatic expansion without the performance of work). It would, therefore, be incorrect to depict it by an adiabatic with unchanging entropy. The process CC_1 can only be included in the pv diagram as an imaginary line; increased entropy is typical of this process.—*Ed.*

pressed air at a temperature higher than that of spontaneous combustion, ignites of its own accord and requires no special devices to ignite it. The injection of the necessary amount of fuel into the cylinder and the process of combustion that begins when the piston is at LDC require a certain amount of time and may take place under varying conditions. The injection of fuel is usually regulated in such a way that combustion takes place at constant pressure. Such engines work exclusively on heavy liquid fuels, since the use of a gaseous

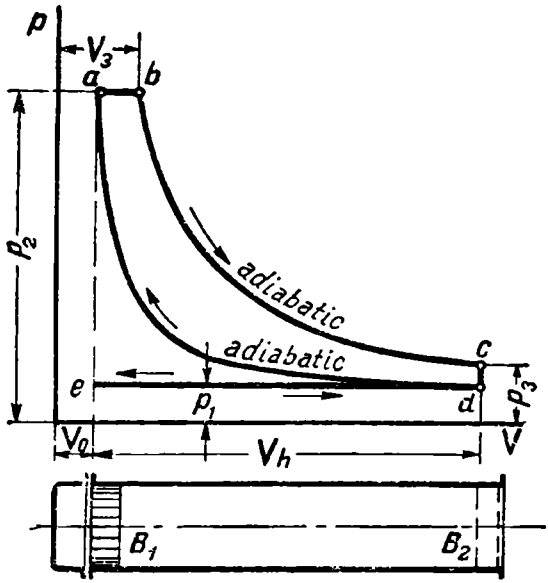


Fig. 7-6

fuel for the cycle presents very considerable practical difficulty. The recent transfer of oil engines to generator gas fuel is connected with their adaptation to work on a cycle with combustion at constant volume.

The theoretical indicator diagram for a four-stroke oil engine working by combustion at constant pressure is given in Fig. 7-6; it works in the following way.

On its first stroke *ed* the piston sucks air at constant pressure p_1 into the cylinder to a volume of V_h. The second stroke compresses it by adiabatic *da* to p_2 - 30-40 ata, and T = = 600°-800° C. At the beginning of the third stroke the necessary amount of liquid fuel is injected by a special pump and ignites as it combines with the superheated air without any sort of artificial ignition, theoretically at

the constant pressure p_2. At point b the supply of fuel is cut off and combustion ceases; the products of combustion expand by the adiabatic bc to the end of the stroke. When the piston reaches RDC the exhaust valve opens and the pressure in the cylinder drops instantaneously according to the vertical line cd from pressure p_3 to the external pressure p_1, and part of the products of combustion expand and leave the cylinder. On its fourth stroke the piston ejects the products of combustion at constant pressure p_1 with a volume of V_h, as shown by the horizontal line de in the dia-

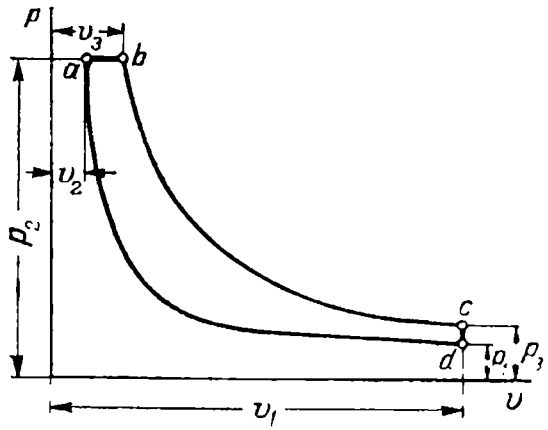


Fig. 7-7

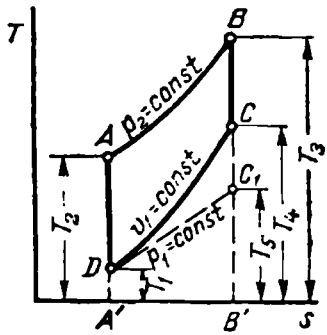


Fig. 7-8

gram. When the piston reaches the end of the stroke the exhaust valve closes and the inlet valve opens allowing air to enter the cylinder and mix with the remains of the products of combustion whose volume is V_0; the whole cycle is then repeated by every four strokes of the piston, i. e., the engine is a four-stroke engine.

For the reasons given above we accept the figure *abcd* conditionally as the indicator diagram of the engine under discussion, as we did for the engine working at constant volume; the diagram, therefore, consists of two adiabatics, an isobar and an isochor (Figs. 7-7 and 7-8).

Adiabatic *da* is the curve showing the change in the state of the air, which is somewhat impure owing to an admixture of products of combustion; adiabatic *bc* shows the change in the state of the products of combustion. With regard to isobar *ab* of the combustion process, we should, strictly speaking, take into consideration the increase in the weight of the

working body in the cylinder as the fuel is injected along line *ab*, so that the weight of the body differs for the two adiabatic processes, *da* and *bc*; but as the weight of the injected fuel is very small compared to the weight of the air in the cylinder, it is permissible to consider the processes *da*, *ab* and *bc* as taking place at unchanging weight and isobar *ab*, therefore, indicates a change of state and not of quantity. The isochor *cd* is imaginary in this cycle as in the preceding one; it serves to close the cycle although it does not actually take place. At the time the pressure in the cylinder is falling along the vertical line *cd*, the products of combustion actually continue to expand outside the cylinder beyond point *c* along adiabatic CC_1 (Fig. 7-8) to pressure p_1, and are then cooled in the air as shown by isobar C_1D. Nevertheless, the cycle *abcd* shows the theoretical use of heat in the engine, since the theoretical work is equal to area *abcd* and the amount of heat expended by the engine is measured as area $ABB'A'$, the equivalent of the heat developed during combustion. In actual fact the work of the engine is less than area *abcd* by an amount equal to the work of the fuel pump, but this is so small compared to the work of the engine cylinder that it may be disregarded.

Assuming that c_p and c_v and, consequently, $k=\frac{c_p}{c_v}$ and R are constant throughout the cycle, the heat imparted to the body during the process of combustion *ab* is found by equation

$$q_1 = c_p (T_3 - T_2),$$

and that given up during process *cd* is found by the equation

$$q_2 = c_v (T_4 - T_1),$$

so that by equation 5-8

$$\eta_t = 1 - \frac{q_2}{q_1} = 1 - \frac{c_v (T_4 - T_1)}{c_p (T_3 - T_2)} = 1 - \frac{1}{k} \times \frac{T_4 - T_1}{T_3 - T_2}.$$

The temperatures T_1, T_2 and T_4 in this last equation may be expressed by T_3 (by equation 4-6) for the isobar *ab*

$$\frac{T_3}{T_2} = \frac{v_3}{v_2} = \rho,$$

where $\rho = \frac{v_3}{v_2}$ is the isobaric expansion ratio, and, therefore,

$$T_2 = \frac{T_3}{\rho}.$$

By equation 4-30 for adiabatic *bc*

$$\frac{T_3}{T_4}=\left(\frac{v_1}{v_3}\right)^{k-1}=\delta^{k-1}$$

where $\delta=\frac{v_1}{v_3}$ is the adiabatic expansion ratio and, therefore,

$$T_4=\frac{T_3}{\delta^{k-1}};$$

for adiabatic *da*

$$\frac{T_2}{T_1}=\left(\frac{v_1}{v_2}\right)^{k-1}=\varepsilon^{k-1}$$

where $\varepsilon=\frac{v_1}{v_2}$ is the adiabatic compression ratio and, therefore,

$$T_1=\frac{T_2}{\varepsilon^{k-1}}=\frac{T_3}{\rho\varepsilon^{k-1}}.$$

The expression for η_t, therefore, will be

$$\frac{T_4-T_1}{T_3-T_2}=\frac{\frac{T_3}{\delta^{k-1}}-\frac{T_3}{\rho\varepsilon^{k-1}}}{T_3-\frac{T_3}{\rho}}=\frac{\frac{1}{\delta^{k-1}}-\frac{1}{\rho\varepsilon^{k-1}}}{1-\frac{1}{\rho}}.$$

The values ρ, ε and δ are interconnected by the simple relation

$$\delta=\frac{v_1}{v_3}=\frac{v_1}{v_2}\times\frac{v_2}{v_3}=\frac{\varepsilon}{\rho}; \qquad (7\text{-}2)$$

i.e., two of them determine the third, so that we may write:

$$\frac{T_4-T_1}{T_3-T_2}=\frac{\frac{\rho^{k-1}}{\varepsilon^{k-1}}-\frac{1}{\rho\varepsilon^{k-1}}}{\frac{\rho-1}{\rho}}=\frac{1}{\varepsilon^{k-1}}\times\frac{\rho^k-1}{\rho-1}$$

and, therefore,

$$\boxed{\eta_t=1-\frac{1}{k}\times\frac{1}{\varepsilon^{k-1}}\times\frac{\rho^k-1}{\rho-1}.} \qquad (7\text{-}3)$$

Thus, we see that the efficiency of the given cycle is determined by the values of ε and ρ, or the values of ε and δ (which is the same thing), i. e., the adiabatic compression and expansion ratios, and that efficiency increases as ε increases and ρ decreases, consequently, as the value of $\delta=\frac{\varepsilon}{\rho}$

increases; in other words, *the higher the adiabatic compression and expansion ratios, the higher the efficiency* η_t. We obtained the same result for the previous cycle in which the compression and expansion ratios had identical values; in the present cycle the adiabatic expansion ratio, δ, is lower than the compression ratio ε. From this we may conclude that *when the compression ratios* ε *are identical, the cycle employing combustion at constant volume is more economical than that employing combustion at constant pressure* because in the latter case the adiabatic expansion ratio (δ) is lower than in the former (ε). The latter type of engine works with a compression ratio $\varepsilon=14$ to 16 and more whereas the former type that works by compressing the fuel mixture does not, as a rule, have an ε that is greater than eight; the efficiency η_t of the cycle employing constant pressure may be as high as 55% whereas that working at constant volume does not usually exceed 50%.

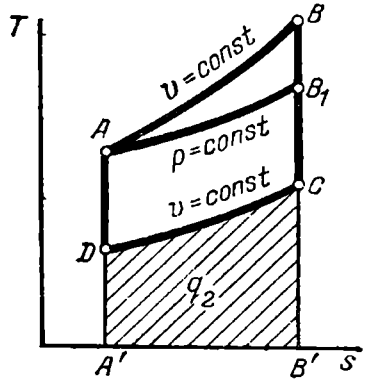


Fig. 7-9

This thesis is fully borne out by the *Ts* diagram. Fig. 7-9 depicts the cycle *ABCD* with combustion at constant volume and cycle AB_1CD with combustion at constant pressure, the adiabatic compression ratio, ε, and the value of q_2 being identical in the two cases.

The efficiency of cycle *ABCD* is

$$\eta_t = 1 - \frac{q_2}{q_1}$$

where q_1 = area $ABB'A'$.

The efficiency of the cycle AB_1CD is

$$\eta_t' = 1 - \frac{q_2}{q_1'}$$

where q_1' = area $AB_1B'A'$; since $q_1 > q_1'$, it is obvious that $\eta_t > \eta_t'$.

However, the comparison of two cycles with an identical ε has no practical significance since an engine with combustion at constant pressure is designed for a greater value of ε than an engine with combustion at constant volume, which

gives the former considerable advantage. It is therefore better to compare cycles with identical maximum pressures and temperatures, i. e., under conditions in which the engines have identical mechanical and thermal stresses as in Fig. 7-10 which shows cycle $ABCD$ with combustion at constant volume and cycle A_1BCD with combustion at constant pressure but with a common point B indicating p_{max} and T_{max} and an identical value of q_2.

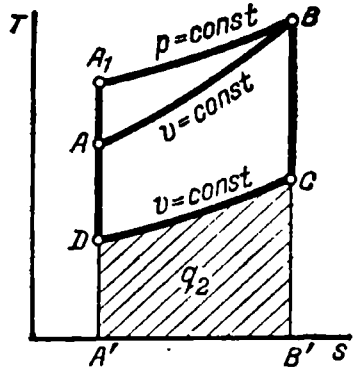


Fig. 7-10

The efficiency of cycle $ABCD$

$$\eta_t = 1 - \frac{q_2}{q_1}$$

where q_1 = area $ABB'A'$.

The efficiency of cycle A_1BCD

$$\eta_t' = 1 - \frac{q_2}{q_1'}$$

where q_1'=area $A_1BB'A'$. Since $q_1' > q_1$, it is obvious that $\eta_t' > \eta_t$.

The cycle under discussion is that of the diesel engines that are widely used both as stationary engines and as marine engines; nowadays diesel engines are being used with great success in locomotives, motor vehicles, tractors and even in aircraft.

7-5. The Combined Combustion Cycle. With a fixed pressure when compression is completed, combustion at constant volume gives a higher efficiency than combustion at constant pressure; for instance, when pressure at the end of the compression stroke is 25 ata, i. e., $\varepsilon = 11.2$ and $\rho = 2.5$, the efficiency of the cycle at constant pressure is 0.46 and at constant volume 0.55. The higher efficiency in the second case, when pressure at the end of the adiabatic expansion is identical, is, however, due to a considerable simultaneous increase in the greatest pressure in the cylinder which, in the first cycle, is the same as the pressure at the end of the compression stroke—in our example, 25 ata, and in the second case it is 85.2 ata, i. e., 3.4 times greater. This greatly increased pressure involves a big increase in the weight of the engine and, therefore, a higher cost so that it is frequently rejected as being irrational. In many cases, however, it has been found

practical to design an engine that works with a combination of the two cycles and which occupies an intermediate place between them. This cycle, known as the cycle with a combined supply of heat or combined combustion cycle was first

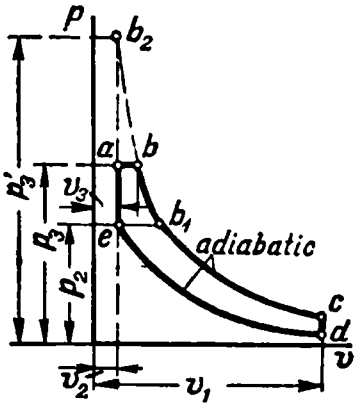


Fig. 7-11

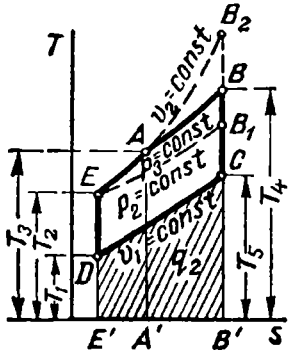


Fig. 7-12

projected and realised by Trinkler, a Russian engineer; it is shown in Figs. 7-11 and 7-12 (cycle *abcde* in the *pv* diagram corresponding to *ABCDE* in the *Ts* diagram). Part of the liquid fuel (the smaller part) is injected into the air compressed along adiabatic *de* exactly when the piston reaches LDC, and combustion takes place theoretically at constant volume *EA* and the remainder, the greater part, is injected into the cylinder during the piston stroke and its combustion takes place at constant pressure along line *AB*. Comparing cycles *ABCDE*, EB_1CD and EB_2CD with an identical compression ratio, ε, we see from the *Ts* diagram that the amount of heat given up, q_2, is identical, which means that the efficiency of the cycle *ABCDE* with a combined supply of heat is greater than that of the cycle EB_1CD but smaller than that of cycle EB_2CD; simultaneously, the maximum pressure of the cycle with combined supply of heat (p_3) is greater than that of cycle EB_1CD (p_2) but less than that of EB_2CD (p_3'). For example:

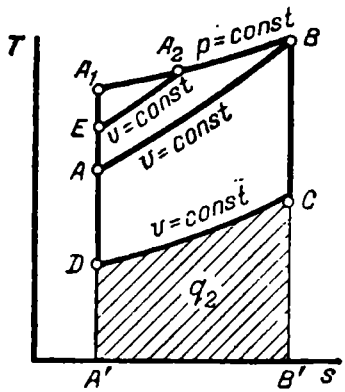


Fig. 7-13

at $p_2=25$ ata and $p_3=36$ ata the efficiency of the cycle with a combined supply of heat is 0.5 as compared with 0.46 for the EB_1CD cycle and 0.55 for the EB_2CD cycle.

A different picture is obtained if we compare cycles with identical maximum pressures and temperatures as in Fig. 7-13 instead of identical compression ratios, ε. We see from the diagram that under these conditions cycle A_1BCD with combustion at constant pressure has the highest efficiency and cycle $ABCD$ with combustion at constant volume has the lowest.

The combined combustion cycle EA_2BCD has an intermediate level of efficiency. The practical significance of the cycle with a combined supply of heat is that it is realised with the same compression ratio ε as the cycle with combustion at constant pressure so that maximum pressure and temperature in the former are greater than in the latter and its efficiency is, therefore, higher.

We shall now evolve the expression for the efficiency of the cycle under discussion.

During process *ea* the heat imparted is represented as area $EAA'E'$ (see Fig. 7-12) and is expressed as

$$q_1' = c_v (T_3 - T_2),$$

and the heat imparted during process *ab*, represented as area $ABB'A'$, is

$$q_1'' = c_p (T_4 - T_3),$$

and the total heat expended on the cycle is

$$q_1 = q_1' + q_1'' = c_v (T_3 - T_2) + c_p (T_4 - T_3).$$

The heat given up during process *cd* is

$$q_2 = c_v (T_5 - T_1),$$

so that the efficiency of the cycle is

$$\eta_t = 1 - \frac{q_2}{q_1} = 1 - \frac{c_v (T_5 - T_1)}{c_v (T_3 - T_2) + c_p (T_4 - T_3)} =$$

$$= 1 - \frac{T_5 - T_1}{T_3 - T_2 + k (T_4 - T_3)}.$$

The temperatures T_1, T_2, T_3 and T_5 in this last equation may be expressed by means of T_4, as in equation 4-6, for the isobar *ab*

$$\frac{T_4}{T_3} = \frac{v_2}{v_1} = \rho$$

where ρ is the isobaric expansion ratio and, consequently,

$$T_3 = \frac{T_4}{\rho}.$$

For the isochor *ea*, by equation 4-2

$$\frac{T_3}{T_2} = \frac{p_3}{p_2} = \lambda,$$

therefore

$$T_2 = \frac{T_3}{\lambda} = \frac{T_4}{\lambda\rho}.$$

By equation 4-30 for adiabatic *de*

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{k-1} = \varepsilon^{k-1},$$

where ε is the adiabatic compression ratio, therefore,

$$T_1 = \frac{T_2}{\varepsilon^{k-1}} = \frac{T_4}{\lambda\rho\varepsilon^{k-1}}.$$

Lastly, for adiabatic *bc*

$$\frac{T_4}{T_5} = \left(\frac{v_1}{v_3}\right)^{k-1} = \delta^{k-1},$$

where δ is the adiabatic expansion ratio, and, since $\delta = \frac{\varepsilon}{\rho}$ (equation 7-2)

$$T_5 = \frac{T_4}{\delta^{k-1}} = \frac{\rho^{k-1} T_4}{\varepsilon^{k-1}}.$$

In which case

$$\eta_t = 1 - \frac{\frac{\rho^{k-1}T_4}{\varepsilon^{k-1}} - \frac{T_4}{\lambda\rho\varepsilon^{k-1}}}{\frac{T_4}{\rho} - \frac{T_4}{\lambda\rho} + k\left(T_4 - \frac{T_4}{\rho}\right)} =$$

$$= 1 - \frac{1}{\varepsilon^{k-1}} \times \frac{\lambda\rho^k - 1}{\lambda - 1 + k\lambda(\rho - 1)}. \qquad (7\text{-}4)$$

Efficiency η_t, as can be seen from equation 7-4, increases with an increase of ε and λ and a decrease of ρ. It is not difficult to establish the fact that with a definite expenditure of fuel on the cycle and a definite compression ratio ε the values of λ and ρ mutually determine one another, i. e., an increase of λ reduces ρ and vice versa. We know that $\lambda=\frac{p_3}{p_2}$, that is, the increase in pressure at the time of the explosive combustion is the greater, the greater the part of the fuel that is ignited at constant volume and, simultaneously, the less the amount of fuel that is ignited at constant pressure and, consequently, the less the time taken for the process of combustion, which means the less the value of ρ. And since the isobaric expansion ratio ρ at a given ε determines the adiabatic expansion ratio δ by the relation $\delta=\frac{\varepsilon}{\rho}$, it may be said, in the final analysis, that *the efficiency of a cycle employing combined combustion, similarly to that of the previous two cycles, is determined by the adiabatic compression ratio, ε, and the expansion ratio, δ, and increases as those values increase.*

The two foregoing cycles are particular cases of a cycle with combined combustion; their efficiency is obtained from equation 7-4 by substituting $\rho=1$ for the cycle at constant volume and $\lambda=1$ for the cycle at constant pressure. The combined combustion cycle is now being used by some internal combustion engine designers.

Chapter Eight

THE AIR COMPRESSOR

8-1. The Working Process of the Reciprocating Compressor. Air at high pressures is extensively used in industry — compressed air engines, pneumatic tools for riveting, drilling and caulking, pneumatic forge hammers, for cleaning castings, etc. Since compressed air is an accumulator of work, it can only be obtained by expending the necessary amount of work in special machines called *compressors*; the latter may be either reciprocating or rotary machines. We shall study the work of a reciprocating compressor as being the simpler of the two.

The cylinder of the compressor, like that of any machine whose piston has translational motion, may be shown in an indicator diagram whose ordinates indicate the pressure in the cylinder at the different positions of the piston and whose area is the magnitude of the work corresponding to the volume of the cylinder for one working process. Fig. 8-1 is a theoretical diagram of this type. As the piston moves from LDC to RDC it sucks in air through an automatically opening suction valve, the volume being equal to that of the cylinder, V_h, at atmospheric pressure p_1, which in our diagram is a section of the horizontal line ab. On the return stroke the piston compresses the air in the cylinder according to curve bc until the pressure in the cylinder attains the value p_2 which is the same as the pressure of the compressed air contained in the reservoir. A force valve then opens automatically and the piston, completing the stroke, forces the air out

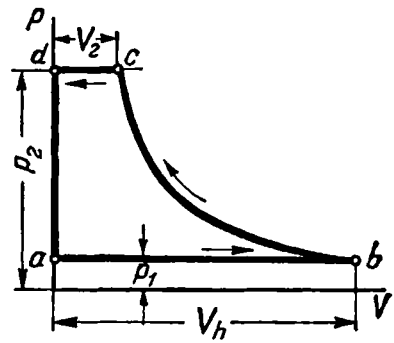


Fig. 8-1

of the cylinder with a volume of V_2 at constant pressure p_2, if the pressure in the reservoir does not change. This period, during which air is being forced out of the cylinder, is depicted by the horizontal line *cd* in the diagram. At the beginning of the next stroke of the piston the suction valve opens, the pressure in the cylinder drops from p_2 to p_1 (in theory, instantaneously, according to the vertical line *da*) and the working process is repeated; it is, therefore, effected by two strokes of the piston so that the compressor is a two-stroke machine. In accordance with the general features of our diagrams, the area *abcd* shows the work expended by the compressor for one revolution of its shaft. At one and the same finite pressure p_2, the finite volume V_2 will vary as the nature of the curve *bc*, i. e., depending on the process of compression; the amount of work expended by the compressor will also differ. In the absence of an exchange of heat the compression curve *bc* will be adiabatic, with its equation pv^k=const. It can be seen that isothermic compression involves an expenditure of work that is smaller by the shaded area *ecd* in diagram 8-2 than adiabatic compression, since the isotherm is closer to the horizontal than the adiabatic. The amount of work expended would not be of any importance if it were returned in full by the subsequent expansion in the instruments employing compressed air. In actual fact, however, before the compressed air reaches the consumer it is cooled by an exchange of heat in the pipes and in the reservoir until it attains the external temperature, i. e., after having been compressed adiabatically it leaves the compressor in the state shown by point *c* and reaches the consumer in the state shown by point *e*. In practice it would, therefore, be better to conduct the process of compression in accordance with the isotherm *be* instead of the adiabatic *bc*. But isothermic compression is difficult to accomplish; the actual compression curve lies between the adiabatic and the isotherm and may be regarded as a polytrope with the equation pv^n= =const in which the exponent n is greater than unity but less than k. This polytropic process of compression is due to

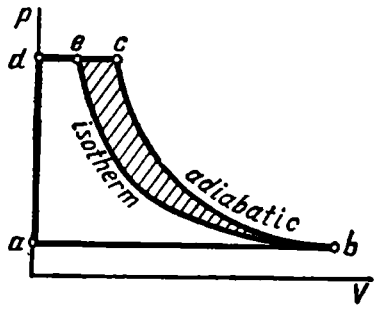


Fig. 8-2

the extraction of heat from the air being compressed which is effected by the use of a water jacket on the cylinder of the compressor.

The work of the compressor for one working process of polytropic compression, L, is area $abcd$ on the indicator diagram (Fig. 8-3) and may be obtained as follows:

L=area $abcd$=area $dcc'o$+ +area $cbb'c'$—area $abb'o$, but

area $dcc'o = p_2V_2$;

area $cbb'c' = \frac{1}{n-1}(p_2V_2 - p_1V_h)$;

area $abb'o = p_1V_h$,

so that

$$L = p_2V_2 + \frac{1}{n-1}(p_2V_2 - p_1V_h) - p_1V_h =$$

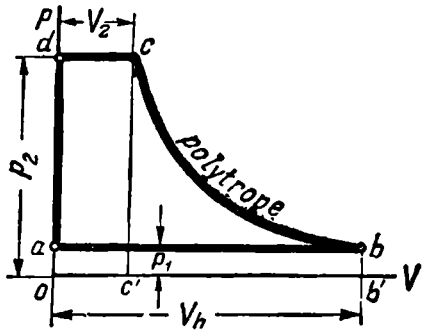


Fig. 8-3

$$= \frac{1}{n-1}(p_2V_2 - p_1V_h) + (p_2V_2 - p_1V_h) =$$

$$= \left(\frac{1}{n-1} + 1\right)(p_2V_2 - p_1V_h) = \frac{n}{n-1}(p_2V_2 - p_1V_h) =$$

$$= \frac{n}{n-1} p_1V_h \left(\frac{p_2}{p_1} \times \frac{V_2}{V_h} - 1\right),$$

and since

$$\frac{V_2}{V_h} = \left(\frac{p_1}{p_2}\right)^{\frac{1}{n}},$$

we finally get

$$L = \frac{n}{n-1} p_1V_h \left[\left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}} - 1\right] \text{ [kgm]}. \qquad (8\text{-}1)$$

Equation 8-1 gives the absolute magnitude of the work of the compressor which, of course, is negative.

The work expended on 1 cum of air in the initial state represented by point b, is

$$L = \frac{n}{n-1} p_1 \left[\left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}} - 1\right] \text{ [kgm-cum]}. \qquad (8\text{-}2)$$

The work expended on 1 cum of air in the final state (point *c*) is

$$L = \frac{n}{n-1} p_1 \frac{V_h}{V_2} \left[\left(\frac{p_2}{p_1} \right)^{\frac{n-1}{n}} - 1 \right] =$$

$$= \frac{n}{n-1} p_1 \left(\frac{p_2}{p_1} \right)^{\frac{1}{n}} \left[\left(\frac{p_2}{p_1} \right)^{\frac{n-1}{n}} - 1 \right] = \frac{n}{n-1} p_1 \left[\frac{p_2}{p_1} - \left(\frac{p_2}{p_1} \right)^{\frac{1}{n}} \right] =$$

$$= \frac{n}{n-1} p_2 \left[1 - \left(\frac{p_2}{p_1} \right)^{\frac{1-n}{n}} \right] =$$

$$= \frac{n}{n-1} p_2 \left[1 - \left(\frac{p_1}{p_2} \right)^{\frac{n-1}{n}} \right] \text{ [kgm-cum]}. \qquad (8\text{-}3)$$

We must not speak of the cycle of a compressor (although this term is often incorrectly used) because the compressor itself only effects the compression process shown by curve *bc*; during the periods of suction *ab* and force pumping *cd* there is no change, theoretically, in the state of the air. Compressors are used to compress other technical gases (oxygen, for example), as well as air, and also in refrigerators to compress vapours (ammonia vapour).

8-2. The Multi-Stage Compressor. At high degrees of compression high temperatures are reached at the end of the process in a single-cylinder compressor which are undesirable from the practical point of view. This can be avoided if the compression is carried out in two or three stages by joining several cylinders in series and cooling the air at the intermediate stages with water jackets as it passes from one cylinder to another.

Fig. 8-4 is a *pV* diagram showing the work of a three-stage compressor. Air is sucked into the first cylinder of a displacement volume V_{h1} at pressure p_1 and is compressed as polytrope *2-3* to pressure p_2 at which it enters the first cooling stage; its temperature is then reduced at constant pressure to that of point *2* and its volume is simultaneously reduced to V_{h2}. This cooling process is shown in the diagram as the horizontal line *3-4*; point *4* lies on an isotherm drawn through point *2*. The area *5-3-2-1* shows the work expended on compression at the first stage.

From the first cooler the air in the state at point *4* is sucked into the second cylinder at the volume of V_{h2} and pressure

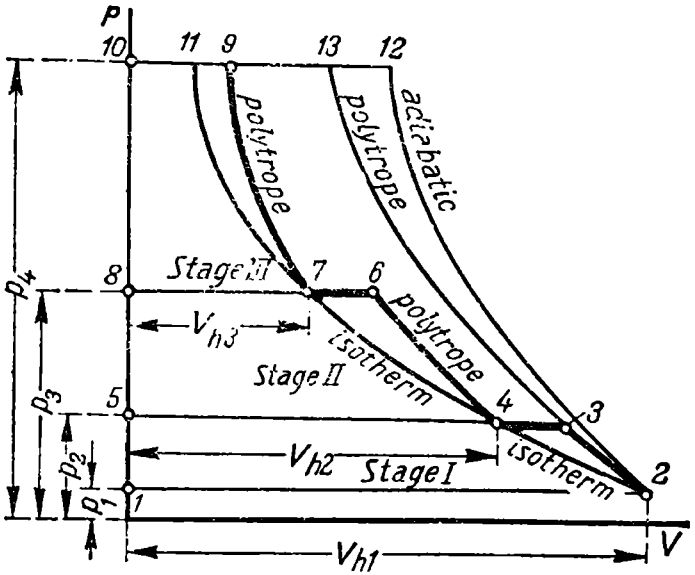


Fig. 8-4

p_2 and compressed according to polytrope *4-6* to pressure p_3 at which it enters the second cooler where its temperature is reduced to that of point *4* (and, consequently, of point *2*) and its volume is reduced to V_{h3}. This second cooling process is shown by the horizontal line *6-7*; point *7* lies on the same isotherm as points *4* and *2*. Area *8-6-4-5* shows the work expended on the second stage of compression.

In the state at point *7* the air is sucked from the second cooler into the third cylinder at volume V_{h3} and pressure p_3 and is again compressed according to polytrope *7-9* to the required pressure p_4, at which it enters the reservoir. Area

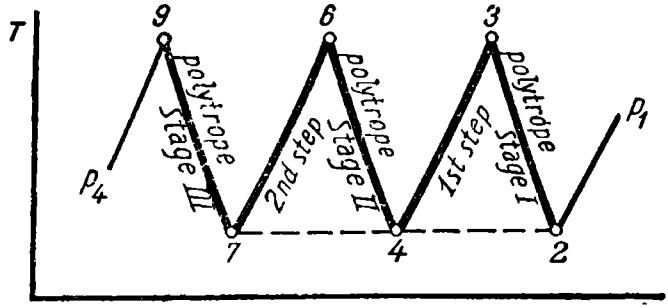


Fig. 8-5

10-9-7-8 shows the work expended on the third stage of compression.

The total work of the three-stage compressor under discussion is the sum of the separate stages, i. e., is equal to the area *10-9-7-6-4-3-2-1*; thus we see that it is much smaller than area *10-12-2-1* of the work of adiabatic compression and smaller than area *10-13-2-1*, the work of polytropic compression in a single-cylinder compressor. It can also be seen that the greater number of stages reduces the work expended on the compressor, bringing the broken line *9-7-6-4-3-2* close to the isotherm *11-2* and at the same time reducing the temperature of the air supplied by the compressor.

Fig. 8-5 is a *Ts* diagram of the process of compression in the machine under discussion.

Chapter Nine

STREAMING OF GASES

9-1. External Work During Streaming. Let it be assumed that gas is moving from left to right at a varying velocity c through a pipe of varying cross-section f with a straight-line axis (Fig. 9-1); the gas fills the pipe and changes its state, determined by the pressure p and the specific volume v, for every different cross-section of the pipe, each section giving a specific value to the constant p, v and c, e. g., cross-section I has p_1, v_1, c_1, cross-section II has p_2, v_2, c_2, etc. The weight of the gas passing through any section of the pipe at any one moment is the same for all cross-sections and does not change with time, i. e.,

$$\frac{f_1 c_1}{v_1} = \frac{f_2 c_2}{v_2} = \frac{fc}{v} = G = \text{const}, \tag{9-1}$$

where G is the *weight of gas expended per second*. The constant weight of the gas flowing through each section at any

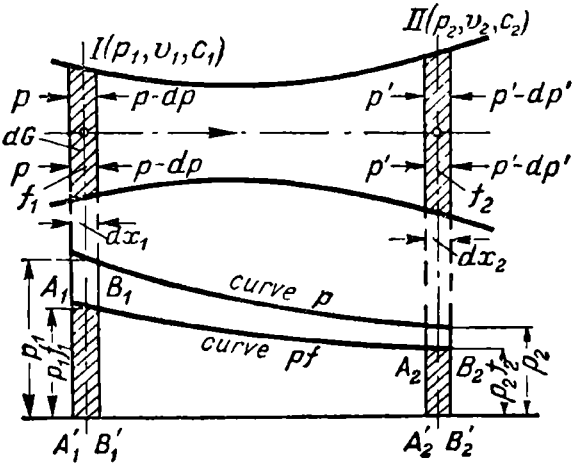


Fig. 9-1

moment determines the continuity of the motion, in accordance with which equation 9-1 is called the *condition of continuity*; the quantity of gas by weight flowing through the pipe in a given time is determined by the motion of the body fixed for the process.

This predetermined continuous movement and the processes connected with it play such an important role in modern heat engineering that we shall have to deal with them in greater detail.

We shall examine the change in state of an elementary mass of the body with a weight of dG enclosed between two infinitely close cross-sections of the pipe at the point of transition from cross-section *I* to cross-section *II*. As far as that mass of the body shown in the shaded strips on Fig. 9-1 is concerned, the pressures on its parallel surfaces are external pressures effected by the layers of the body to the left and right, and in the general case the pressures on the two sides are different and are balanced by the pressures on that layer of the body under discussion. In the particular case, Fig. 9-1, pressure p is exerted from left to right, so that the external specific pressure on the elementary mass is greater from the left than from the right. The full pressure in the cross-sections of the pipe is determined by the product of p and f (the cross-sectional area) so that the value of pf throughout the length of the pipe depends not only on the curve of p values but also on the shape of the pipe.

The external pressure exerted on the left-hand surface does the work expended on moving the body; the external pressure on the right-hand surface, being opposed to the direction of the movement, has the character of resistance and the body performs work in overcoming it; in respect of the body the former work is negative and the latter positive; the algebraic sum of the two types of work is nothing more than the external work necessary to stream the gas. Let us call this sum l' for 1 kg of the body between cross-sections *I* and *II*; for an elementary mass dG the work will be $dG \times l'$. From Fig. 9-1 it follows that the work of the external pressure on the left-hand surface is measured as the area $A_1A_2A_2'A_1'$ and that on the right-hand surface as $B_1B_2B_2'B_1'$ and the work $dG \times l'$ as the difference in the areas, i. e.,

$$dG \times l' = \text{area } B_1B_2B_2'B_1' - \text{area } A_1A_2A_2'A_1' =$$
$$= \text{area } A_2B_2B_2'A_2' - \text{area } A_1B_1B_1'A_1',$$

i. e., the difference in the shaded areas in the lower part of Fig. 9-1. When dx_1 and dx_2 are infinitely small

$$\text{area } A_2B_2B_2'A_2' = p_2f_2dx_2 = p_2dV_2 = p_2dGv_2$$

and

$$\text{area } A_1B_1B_1'A_1' = p_1f_1dx_1 = p_1dV_1 = p_1dGv_1,$$

where dV_1 and dV_2 are the volumes of the shaded mass of the gas at the beginning and end of the change of state between cross-sections *I* and *II*;

v_1 and v_2 are the corresponding specific volumes.

Thus,

$$dG \times l' = p_2dGv_2 - p_1dGv_1 = dG\,(p_2v_2 - p_1v_1)$$

and, therefore,

$$l' = p_2v_2 - p_1v_1,$$

and for an infinitely small change of state

$$\underline{dl' = d\,(pv).} \tag{9-2}$$

The equation of the first law of thermodynamics, as the law of the conservation of energy applied to the process of streaming with a variable velocity, c, must be complemented in its right-hand part on account of the change in the kinetic energy of the visible motion of the body, which, for 1 kg of the body in the elementary process, is $d\left(\frac{c^2}{2g}\right)$ so that the equation becomes

$$dq = du + Adl' + Ad\left(\frac{c^2}{2g}\right); \tag{9-3}$$

substituting $dl' = d\,(pv)$ from equation 9-2 we get:

$$dq = du + Ad\,(pv) + Ad\left(\frac{c^2}{2g}\right) = d\,(u + Apv) + Ad\left(\frac{c^2}{2g}\right) =$$

$$\underline{= di + Ad\left(\frac{c^2}{2g}\right).} \tag{9-4}$$

Equation 9-4 is basic for a stream of gas or vapour and is true for both the reversible and irreversible processes of ejection. It may be formulated as follows: *in the general case, the heat imparted to the body during streaming is expended in two directions—part of it goes to increase the enthalpy of the body and the remainder to increase the internal kinetic energy, i. e., the velocity of the stream.*

9-2. The Available Work of a Streaming Process. In addition to equation 9-4, equation 2-10 retains its importance for a reversible streaming process:

$$dq = du + A dl,$$

where $dl = p\,dv$ is the elementary work of the expansion of the body; combining equations 2-10 and 9-3, we get

$$dl = dl' + d\left(\frac{c^2}{2g}\right),$$

i. e., the work of expansion during streaming at variable velocity results in the performance of external work and in an increase in the external kinetic energy of the body.

The difference in the two amounts of work dl and dl' is

$$dl_0 = dl - dl' = d\left(\frac{c^2}{2g}\right), \qquad (9\text{-}5)$$

i. e., the increased kinetic energy of the body is a kind of *available work* that can be used for some purpose; in steam turbines, for example, steam is ejected at considerable velocity, obtained as a result of expansion, through the curved blades of the rotor, loses its velocity and at the expense of reduced internal kinetic energy turns the shaft of the turbine, i. e., performs work.

By inscribing $dl = p\,dv$ and $dl' = d(pv)$ in equation 9-5, we get

$$dl_0 = d\left(\frac{c^2}{2g}\right) = p\,dv - d(pv) = p\,dv - p\,dv - v\,dp = -v\,dp. \qquad (9\text{-}6)$$

The same result may be obtained by combining equation 9-4 and equation 3-35:

$$dq = di + Ad\left(\frac{c^2}{2g}\right) = di - Av\,dp;$$

where p=const., i. e., $dp=0$ and $dl_0=0$; $dl_0>0$ only when $dp<0$, i. e., *the essential condition under which work may be obtained is a reduction in pressure.*

Equation 9-6 can be written in this way:

$$\frac{c}{g}\,dc = -v\,dp,$$

from which we see that dc and dp have unlike signs, i. e., in a reversible process *an increase in the velocity is closely con-*

nected with a reduction in pressure and, vice versa, a reduction in velocity is accompanied by an increase in pressure.

Let it be assumed that pressure changes according to the curve *ab* (Fig. 9-2); since the shaded area represents

$$-v\,dp = dl_0$$

it is obvious that the available work of the streaming process *ab* is

$$l_0 = \int_{p_1}^{p_2} -v\,dp = \int_{p_2}^{p_1} v\,dp$$

and is represented by the area *abb"a"* enclosed between the curve of the process, the axis of the ordinate and the highest and lowest isobars. The work of expansion $l = \int_{v_1}^{v_2} pdv$ is represented, as usual, by the area *abb'a'* enclosed between the curve of the process, the axis of the abscissa and the extreme isochors.

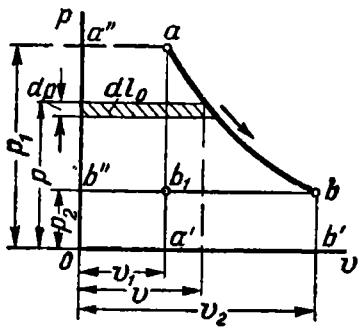


Fig. 9-2

The result may be obtained in another way, by integrating equation 9-6; thus, for process *ab* we get

$$l_0 = \int_{v_1}^{v_2} p\,dv - \int_{p_1}^{p_2} d(pv) = \int_{v_1}^{v_2} p\,dv - p_2v_2 + p_1v_1 =$$

$$= \text{area } abb'a' - \text{area } b"bb'o + \text{area } a"aa'o = \text{area } abb"a".$$

If the curve *ab* is a polytrope expressed by the equation $pv^n = \text{const}$, the work of expansion, as we know, is

$$l = \frac{1}{n-1}(p_1v_1 - p_2v_2),$$

and, since, by equation 9-2

$$l' = p_2v_2 - p_1v_1$$

it follows that

$$l_0 = l - l' = \frac{1}{n-1}(p_1v_1 - p_2v_2) - p_2v_2 + p_1v_1 =$$

$$= \frac{n}{n-1}(p_1v_1 - p_2v_2) = \underline{nl}. \qquad (9\text{-}7)$$

The available work may be greater or less than the work of expansion, depending on the exponent of the polytrope; they may also be equal. Thus, for example, in cases of isothermic expansion of a gas, $l_0 = l$, since $n = 1$ and, consequently, $l' = 0$; this is obvious, because when $t = \text{const}$, pv is also constant, i. e., $dl' = d(pv) = 0$. In the case of the adiabatic expansion of air, the available work is 40% greater than the work of expansion because $n = 1.4$; $l' < 0$, therefore external work is expended. If the change takes place according to isochor ab_1 (Fig. 9-2) the work of expansion is $l = 0$; nevertheless we have available work, l_0 which can be measured on the basis of area $ab_1b''a''$; this means that $l' < 0$ and in value is equal to l_0, in which case, by equation 9-2

$$l' = (p_2 - p_1)v_1 = -(p_1 - p_2)v_1 = -l_0.$$

To conclude from the equation $l_0 = nl$ that $l_0 = 0$ because $l = 0$ would, as we see, be a mistake, since for isochor $n = \pm\infty$, and the product, $nl = \infty \times 0$ is mathematically indefinite.

It follows from equation 9-4 that

$$Ad\left(\frac{c^2}{2g}\right) = \underline{Adl_0 = dq - di;} \qquad (9\text{-}8)$$

i. e., *the available work is obtained, in the general case, by imparting heat to the body from an external source and by decreasing its enthalpy (heat content) at constant pressure.* For a finite process

$$\boxed{Al_0 = q + i_1 - i_2,} \qquad (9\text{-}9)$$

where i_1 and i_2 are the values of the enthalpy at the beginning and end of the process. Equations 9-8 and 9-9 as well as equation 9-4 are true for both reversible and irreversible processes.

In the general case the available work according to equation 9-9 is

$$Al_0 = q + i_1 - i_2.$$

In the Ts diagram the amount of heat, q, is represented by the area under the curve of the process. For an *ideal gas*, by equation 3-38, we have

$$di = c_p dT$$

and, therefore,

$$i_1 - i_2 = \int_{T_2}^{T_1} c_p dT,$$

i. e., the difference in the enthalpy of the gas is equal to the amount of heat imparted at constant pressure within the given temperature limits; this difference is independent of the actual value of the pressure and is represented in the Ts system by the area under any isobar. If, therefore, the gas process is depicted in the system Ts by the curve AB (Fig. 9-3), by extending a horizontal line from the final point B to cut an isobar drawn through point A at point C we get the difference $(i_1—i_2)$ as the area $CAA'C'$ and the amount of heat q as area $ABB'A'$ and, consequently, the available work Al_0 as the area $CABB'C'$, the sum of the areas. *This is true only of reversible streaming processes since it is only for these that the area below the curve in the system Ts shows the amount of heat, q.*

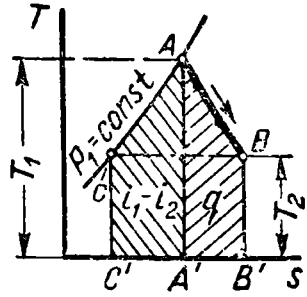


Fig. 9-3

9-3. The Adiabatic Streaming Process. Critical Relation of Pressures. Equation 9-8 applied to adiabatic processes has a simple form

$$A\,dl_0 = -di,$$

i. e., the available work is obtained in a process of adiabatic expansion by a drop in the heat content; for a finite process this is

$$Al_0 = i_1 - i_2. \qquad (9\text{-}10)$$

The difference in heat content at the beginning and end of the process is known as the *heat drop* so that equation 9-10 may be formulated as follows: the available work in a process of adiabatic expansion is equal to the heat drop.

Figs. 9-4 and 9-5 depict the adiabatic process in a pv diagram; area $abb''a''$ (Fig. 9-4) is the amount of available work, the equivalent of the heat drop $(i_1—i_2)$, and area $abb'a'$ below the adiabatic curve (Fig. 9-5) is the work of expansion, the equivalent of the difference in the internal energy $(u_1—u_2)$, the former being k times greater than the latter, where k is the adiabatic index.

Integrating equation 9-5

$$dl_0 = d\left(\frac{c^2}{2g}\right),$$

we get, for the general case,

$$l_0 = \frac{c_2^2 - c_1^2}{2g}$$

where c_1 and c_2 are the magnitudes of the velocity of the gas or vapour at the beginning and end of the process; hence,

$$c_2 = \sqrt{c_1^2 + 2gl_0}.$$

In a number of adiabatic processes of streaming the initial velocity c_1 is so small as compared with c_2 that it may be

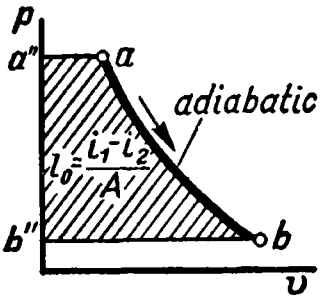


Fig. 9-4

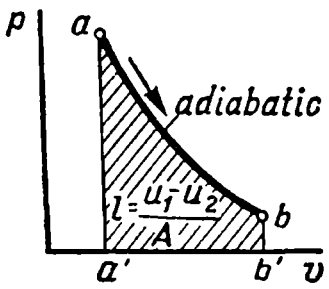


Fig. 9-5

completely ignored; in such cases, i. e., when $c_1=0$, the velocity at the end of the ejection is

$$c = \sqrt{2gl_0}; \qquad (9\text{-}11)$$

for the adiabatic process, applying equation 9-10,

$$c = \sqrt{2g\frac{i_1 - i_2}{A}} = \sqrt{2 \times 9.81 \times 427\,(i_1 - i_2)} =$$

$$= \sqrt{8{,}380\,(i_1 - i_2)} = \underline{91.5\sqrt{i_1 - i_2} = 91.5\sqrt{h},} \qquad (9\text{-}12)$$

where $h = i_1 - i_2$ is the heat drop. It must here be mentioned that the velocity of adiabatic streaming with a drop of h Cal/kg of heat is the same as the velocity of free fall from a height of $H = 427\,h$ metres; this justifies the term "heat drop" for the magnitude h.

If we express the adiabatic curve by an equation of the $pv^k = \text{const}$ type, where k is a constant we get, by combining equations 9-7 and 4-29

$$l_0 = kl = \frac{k}{k-1} p_1 v_1 \left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}\right];$$

making the necessary substitution in equation 9-11, we get

$$c = \sqrt{2g \frac{k}{k-1} p_1 v_1 \left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}\right]}. \qquad (9\text{-}13)$$

By analogy with this equation, the velocity in a cross-section of the pipe at pressure p

$$c = \sqrt{2g \frac{k}{k-1} p_1 v_1 \left[1 - \left(\frac{p}{p_1}\right)^{\frac{k-1}{k}}\right]}. \qquad (9\text{-}14)$$

The adiabatic process of streaming is of great importance to the theory of turbines and must, therefore, be studied in detail.

Let it be assumed that a gas or vapour in an initial state p_1, v_1 is streamed through a cone-shaped nozzle, the cross-section of whose outlet is f, into a medium at a pressure $p < p_1$ and expands adiabatically (Fig. 9-6). Assuming that the expansion takes place in the nozzle from pressure p_1 to pressure p, the latter will be the pressure at the outlet and the velocity of the stream, by equation 9-14, will be

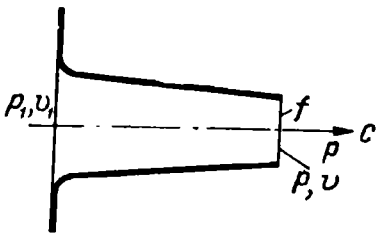


Fig. 9-6

$$c = \sqrt{2g \frac{k}{k-1} p_1 v_1 \left[1 - \left(\frac{p}{p_1}\right)^{\frac{k-1}{k}}\right]},$$

and the weight of the gas expended will be

$$G = \frac{fc}{v}$$

where v — the specific volume of the gas at the outlet (i.e., at pressure p), obtained from the adiabatic equation

$$pv^k = p_1 v_1^k$$

and is

$$v = v_1 \left(\frac{p_1}{p}\right)^{\frac{1}{k}}.$$

Substituting the values of c and v in the expression for the expenditure of gas G we get

$$G = f \times \frac{1}{v_1}\left(\frac{p}{p_1}\right)^{\frac{1}{k}} \sqrt{2g\frac{k}{k-1}p_1v_1\left[1-\left(\frac{p}{p_1}\right)^{\frac{k-1}{k}}\right]} =$$

$$= f\sqrt{2g\frac{k}{k-1}\times\frac{p_1}{v_1}\left[\left(\frac{p}{p_1}\right)^{\frac{2}{k}}-\left(\frac{p}{p_1}\right)^{\frac{k-1}{k}}\right]}. \quad (9\text{-}15)$$

We see from equation 9-15 that with the given original state of the gas (p_1, v_1) and the cross-section of the nozzle f, the expenditure of gas G depends on p, the pressure of the medium into which the gas is streamed.

It will not be difficult to convince ourselves that under these conditions the expenditure G will be maximum when the definite value of p is that of p_{cr}, the critical pressure, which we obtain by taking the first product of the expression in square brackets and reducing it to zero. We get:

$$\frac{d}{dp}\left[\left(\frac{p}{p_1}\right)^{\frac{2}{k}}-\left(\frac{p}{p_1}\right)^{\frac{k+1}{k}}\right]=\frac{2}{k}\left(\frac{p}{p_1}\right)^{\frac{2}{k}-1}-$$

$$-\frac{k+1}{k}\left(\frac{p}{p_1}\right)^{\frac{k+1}{k}-1}=\frac{2}{k}\left(\frac{p}{p_1}\right)^{\frac{2-k}{k}}-\frac{k+1}{k}\left(\frac{p}{p_1}\right)^{\frac{1}{k}}=0.$$

Therefore,

$$\frac{2}{k}\left(\frac{p}{p_1}\right)^{\frac{2-k}{k}}=\frac{k+1}{k}\left(\frac{p}{p_1}\right)^{\frac{1}{k}},$$

or,

$$\frac{2}{k+1}=\left(\frac{p}{p_1}\right)^{\frac{1}{k}\frac{2-k}{k}}=\left(\frac{p}{p_1}\right)^{\frac{k-1}{k}},$$

whence,

$$\frac{p}{p_1}=\frac{p_{cr}}{p_1}=\left(\frac{2}{k+1}\right)^{\frac{k}{k-1}}$$

and

$$p_{cr}=\left(\frac{2}{k+1}\right)^{\frac{k}{k-1}}p_1.$$

We can establish the fact that the function in square brackets actually has the maximum value when $p=p_{cr}$ by taking its second derivative, i. e.,

$$\frac{d}{dp}\left[\frac{2}{k}\left(\frac{p}{p_1}\right)^{\frac{2-k}{k}}-\frac{k+1}{k}\left(\frac{p}{p_1}\right)^{\frac{1}{k}}\right]=$$

$$=\frac{2}{k}\times\frac{2-k}{k}\left(\frac{p}{p_1}\right)^{\frac{2-k}{k}-1}-\frac{k+1}{k}\times\frac{1}{k}\left(\frac{p}{p_1}\right)^{\frac{1}{k}-1}$$

and including in it

$$\frac{p}{p_1}=\left(\frac{2}{k+1}\right)^{\frac{k}{k-1}},$$

so that we get

$$\frac{2}{k}\times\frac{2-k}{k}\left(\frac{2}{k+1}\right)^{\frac{2-2k}{k}\times\frac{k}{k-1}}-\frac{k+1}{k}\times\frac{1}{k}\left(\frac{2}{k+1}\right)^{\frac{1-k}{k}\times\frac{k}{k-1}}=$$

$$=\frac{2(2-k)}{k^2}\left(\frac{2}{k+1}\right)^{-2}-\frac{k+1}{k^2}\left(\frac{2}{k+1}\right)^{-1}=$$

$$=\frac{2(2-k)}{k^2}\times\left(\frac{k+1}{2}\right)^2-\frac{k+1}{k^2}\times\frac{k+1}{2}=\frac{2(2-k)(k+1)^2}{4k^2}-$$

$$-\frac{(k+1)^2}{2k^2}=\frac{(k+1)^2}{2k^2}(2-k-1)=\frac{(k+1)^2}{2k^2}(1-k)<0,$$

i. e., the function actually has the maximum value.

When $k=1.4$, $\frac{p_{cr}}{p_1}=0.528$ for diatomic gases. When $p=p_1$, G will equal zero (by equation 9-15), which is perfectly natural; a reduction in the pressure, p, of the medium gives a greater G, but only within certain limits; to be exact, we get G_{max} when $p-p_{cr}=0.528\ p_1$. A further reduction of p would decrease G, and when $p=0$ equation 9-15 gives us $G=0$, i. e., the streaming of the gas ceases. The dependence of G on p in equation 9-15 is shown graphically in Fig. 9-7 as the parabola *oba*. The reduction of the expenditure G at $p<p_{cr}$ by curve *bo* is as improbable in practice as its increase is natural by curve *ab* when the pressure is reduced from p to p_{cr}. It has been established by experiment that the expenditure through a tapered nozzle (Fig. 9-6) is actually maximum at $p=p_{cr}$, but it is typical of this case that the further reduction of the pressure of the medium to $p<p_{cr}$ does not affect the expenditure; in other words, when $p\leqslant p_{cr}$

the expenditure is $G=G_{max}=$const, so that the actual change in G is according to the curve *abc* (Fig. 9-7).

A hypothesis has been put forward to explain this disagreement between theory and reality; it is held that expansion to a pressure lower than p_{cr} cannot be obtained in a tapered nozzle no matter how low the pressure p of the me-

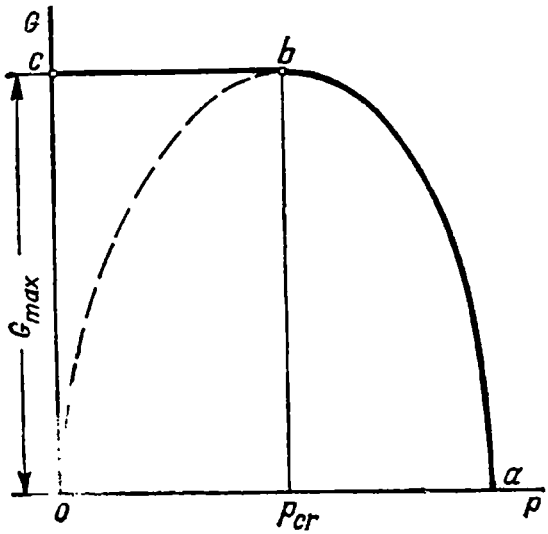


Fig. 9-7

dium into which the gas is streamed. According to this hypothesis the pressure of the medium $p \leqslant p_{cr}$ and the expenditure of gas $G=G_{max}=$const. The hypothesis has been confirmed experimentally. The same results may be obtained by a detailed theoretical study of the adiabatic streaming process.

The condition for uninterrupted motion (equation 9-1) may be written:

$$fc = Gv,$$

where f—the area of a cross-section of the nozzle in sqm;

c —the velocity in mps;

v —the specific volume of the body in that cross-section, cum-kg;

G —the constant expenditure of the body in the nozzle in kgm/sec.

Differentiating this equation we get:

$$f\,dc + c\,df = G\,dv,$$

and, dividing by fc, we get,

$$\frac{dc}{c}+\frac{df}{f}=\frac{G\,dv}{fc}=\frac{dv}{v},$$

whence,

$$\frac{df}{f}=\frac{dv}{v}-\frac{dc}{c}. \tag{9-16}$$

This equation is obviously the condition of continuity in its differential form.

If there is no exchange of heat, i. e., in the case of adiabatic expansion, we may assume that

$$pv^k=\text{const},$$

whence, by differentiation

$$pkv^{k-1}\,dv+v^k\,dp=0,$$

and, dividing by v^k

$$pk\frac{dv}{v}+dp=0$$

and,

$$\frac{dv}{v}=-\frac{1}{k}\times\frac{dp}{p}.$$

Furthermore, by equation 9-6

$$d\left(\frac{c^2}{2g}\right)=-v\,dp,$$

i. e.,

$$\frac{c\,dc}{g}=-v\,dp,$$

and, dividing by c^2

$$\frac{dc}{gc}=-\frac{v\,dp}{c^2}$$

and, therefore,

$$\frac{dc}{c}=-\frac{gv}{c^2}dp.$$

Substituting these values of $\frac{dv}{v}$ and $\frac{dc}{c}$ in equation 9-16, we get

$$\frac{df}{f}=-\frac{1}{k}\times\frac{dp}{p}+\frac{gv}{c^2}dp=\left(\frac{gv}{c^2}-\frac{1}{kp}\right)dp. \tag{9-17}$$

Let us study this equation: during adiabatic expansion the pressure drops and velocity increases in connection with it, i. e., in the direction of the motion $dp<0$, and, therefore, the sign of df depends on the sign of the expression in brackets in the right-hand part of equation 9-17, that is, $fd<0$; in other words, the cross-section of the nozzle is tapered in the direction of the motion if $\frac{gv}{c^2}>\frac{1}{kp}$, that is, if $c<\sqrt{gk\ pv}$, and tapers in the opposite direction if $\frac{gv}{c^2}<\frac{1}{kp}$, that is, if $c>\sqrt{gk\ pv}$. It will be remembered from physics, however, that $c=\sqrt{gk\ pv}$ is the velocity of sound in a gas or vapour at pressure p and volume v; for the gradually increasing velocity to be less than the velocity of sound corresponding to the state of the body at the given moment, the nozzle must taper in the direction of the stream; for the velocity of the body to exceed the velocity of sound the nozzle must expand in the direction of the stream. The point at which the narrowing section of the nozzle changes to an expanding section will obviously be the narrowest section $f_{\min}$ and the velocity in it will be that of sound.

In order to prevent any misunderstanding or an incorrect understanding it must be perfectly clear that, since the velocity of sound is equal to $\sqrt{gk\ pv}$, every different cross-section of the nozzle will, generally speaking, have its own velocity of sound determined by the values of p and v at that cross-section. During adiabatic expansion, the pressure drops and the volume increases in the direction of the stream so that the product of p and v, and, consequently, the velocity of sound, decreases. From this it will be understood that if the velocity of the stream is equal to that of sound in the narrowest part of the nozzle, the increasing velocity of the flow will be greater than the decreasing velocity of sound as the nozzle expands.

If, therefore, the velocity of the stream, corresponding to the heat drop $h=i_1-i_2$ and equal to (equation 9-12) $c = 91.5\sqrt{h}$, is not greater than the velocity of sound in a gas or vapour in its final state, the nozzle must taper towards the outlet, and the cross-section at the outlet will be the smallest. If the velocity c is greater than that of sound the nozzle must first narrow and then widen towards the outlet; a velocity higher than that of sound cannot be obtained in the narrowing nozzle so that the heat drop, h, cannot be com-

pletely used and converted into its equivalent kinetic energy in the gas stream.

In order to decide the shape of the longitudinal cross-section of the nozzle or channel for each individual case it is first necessary to know whether there will be a velocity in the nozzle that is the velocity of sound and, if there is, compare it to the velocity that corresponds to the given heat drop h. If there is a velocity equal to the velocity of sound in the nozzle it will be in its narrowest part where f_{min}, in which there will be set up a critical pressure which we shall call p_{cr}; let us find this pressure. From equation 9-15, the equation of continuity in its detailed form, the magnitude of the cross-section f, which corresponds to the pressure p, with the given expenditure of gas G, will be

$$f = \frac{G}{\sqrt{2g\frac{k}{k-1} \times \frac{p_1}{v_1}\left[\left(\frac{p}{p_1}\right)^{\frac{2}{k}} - \left(\frac{p}{p_1}\right)^{\frac{k+1}{k}}\right]}}. \qquad (9\text{-}18)$$

The variables in equation 9-18 are the values f and p; thus there is a pressure which corresponds to every cross-section, and, by equation 9-14, for each pressure there is a corresponding velocity c. The velocity of sound, as we have said, can only be attained in the cross-section f_{min}; in this part of the nozzle, therefore, the pressure $p = p_{cr}$ is reached. We find this pressure in the usual way, establishing the conditions under which $f = \min$, knowing that the root of the denominator of the right-hand part of the equation will give the maximum.

We have already seen that the conditions are satisfied when

$$\boxed{\frac{p}{p_1} = \frac{p_{cr}}{p_1} = \left(\frac{2}{k+1}\right)^{\frac{k}{k-1}},} \qquad (9\text{-}19)$$

and, therefore,

$$p_{cr} = \left(\frac{2}{k+1}\right)^{\frac{k}{k-1}} p_1. \qquad (9\text{-}20)$$

We see, therefore, that pressure p_{cr} which conditions the existence of a velocity equal to that of sound in the nozzle is fully determined by the initial pressure of the gas or vapour, p_1, and the adiabatic index k. The relation $\frac{p_{cr}}{p_1}$ is called the critical relation of pressures for streaming; we have seen in equation 9-19 that for diatomic gases when $k=1.4$, it is

$$\frac{p_{cr}}{p_1}=0.528.$$

The critical velocity, c_{cr}, that corresponds to the critical pressure, p_{cr}, is found from equation 9-14

$$c=\sqrt{2g\frac{k}{k-1}p_1v_1\left[1-\left(\frac{p}{p_1}\right)^{\frac{k-1}{k}}\right]}$$

by substituting in it $\frac{p}{p_1}=\frac{p_{cr}}{p_1}$ from equation 9-19, so that

$$c_{cr}=\sqrt{2g\frac{k}{k-1}p_1v_1\left(1-\frac{2}{k+2}\right)}=$$

$$=\sqrt{2g\frac{k}{k-1}p_1v_1\frac{k-1}{k+1}}=\underline{\sqrt{2g\frac{k}{k+1}p_1v_1}}. \qquad (9\text{-}21)$$

Thus, we see that it is fully determined by the initial state of the gas and the adiabatic index k; in particular, for diatomic gases $c_{cr}=3.38\sqrt{p_1v_1}$, where the pressure p_1 is in ksqm. For ideal gases, $p_1v_1=RT_1$, so that $c_{cr}=3.38\sqrt{RT_1}$, i. e., the velocity c_{cr} increases with an increase in the initial temperature and differs for different gases; for air at 200° C, for example,

$$c_{cr}=3.38\sqrt{29.27\times473}=398 \text{ m/sec}$$

and at 1,000° C

$$c_{cr}=3.38\sqrt{29.27\times1{,}273}=655 \text{ m/sec}.$$

Cross-section f_{min}, which corresponds to c_{cr}, is obtained from equation 9-18 by including in it $\frac{p}{p_1} = \frac{p_{cr}}{p_1}$ from equation 2-19

$$f_{min} = \frac{G}{\sqrt{2g\frac{k}{k-1}\times\frac{p_1}{v_1}\left[\left(\frac{2}{k+1}\right)^{\frac{k}{k-1}\times\frac{2}{k}} - \left(\frac{2}{k+1}\right)^{\frac{k}{k-1}\times\frac{k+1}{k}}\right]}} =$$

$$= \frac{G}{\sqrt{2g\frac{k}{k-1}\times\frac{p_1}{v_1}\left(\frac{2}{k+1}\right)^{\frac{2}{k-1}}\left[1-\left(\frac{2}{k+1}\right)^{\frac{k+1}{k-1}-\frac{2}{k-1}}\right]}} =$$

$$= \frac{G}{\left(\frac{2}{k+1}\right)^{\frac{1}{k-1}}\sqrt{2g\frac{k}{k-1}\times\frac{p_1}{v_1}\left(1-\frac{2}{k+1}\right)}} =$$

$$= \frac{G}{\left(\frac{2}{k+1}\right)^{\frac{1}{k-1}}\sqrt{2g\frac{k}{k+1}\times\frac{p_1}{v_1}}}, \qquad (9\text{-}22)$$

i e., it is fully determined from the initial state and the expenditure of gas. In particular, for diatomic gases, when $k = 1.4$

$$f_{min} = \frac{G}{2.15\sqrt{\frac{p_1}{v_1}}} \text{ sqm.} \qquad (9\text{-}23)$$

If the adiabatic ab in the system pv (Fig. 9-8) is given, we may, by determining a number of pressures p_x between the

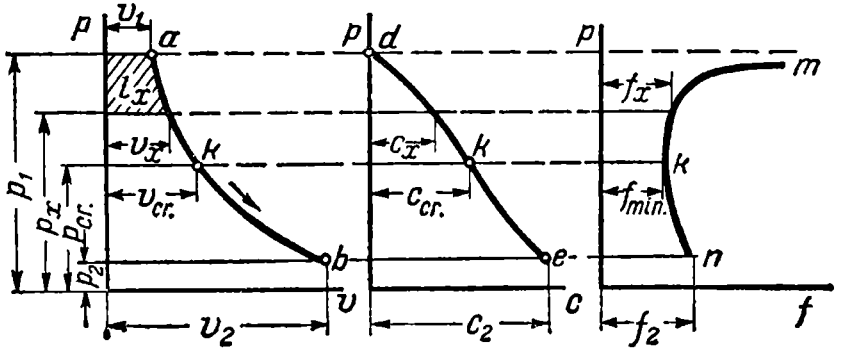


Fig. 9-8

limits p_1 and p_2, find the velocity of the stream $c_x=\sqrt{2gl_x}$, where l_x is the available work obtained from the expansion from p_1 to p_x, represented by the shaded area, and by then using this velocity c_x as the abscissa in the system pc may obtain the curve de which shows the dependence of velocity on pressure in the given cross-section. Each value of the pressure p_x has a corresponding velocity c_x and a specific volume v_x, and, therefore, a definite cross-section area $f_x=G\frac{v_x}{c_x}$ where G is the weight of gas or vapour expended per second. By including in the diagram the paired values v_x and c_x and employing the value f_x as the abscissa of the system pf we get the curve mkn for the general case. In accordance with all that has been said above, when p_2 is less than p_{cr}, i. e., when c_2 is greater than c_{cr}, the nozzle at first narrows and then widens in the direction of the motion, and the smallest diameter f_{min} has the corresponding p_{cr} and c_{cr} which may be determined by equations 9-20 and 9-21. The lower the pressure p_2, and, therefore, the higher the velocity of ejection c_2, the greater the cross-sectional area of the outlet f_2 with f_{min} unchanged. The cross-sectional area f_1, the beginning of the nozzle in the case shown in Fig. 9-8, is infinitely great since the initial velocity c_1 is taken as zero.

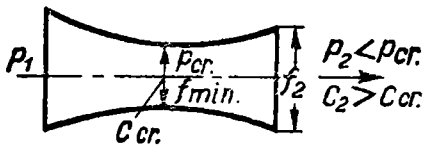


Fig. 9-9

At first glance it seems somewhat strange that it is necessary to widen the nozzle in the direction of the stream in order to obtain velocities greater than c_{cr}, but a closer study of the process of streaming will show that this can be explained in full. The fact of the matter is that at pressures greater than p_{cr}, as pressure is reduced, the velocity increases at a greater rate than the specific volume increases, so that $f_x=G\frac{v_x}{c_x}$ becomes smaller; beginning from the pressure p_{cr} the specific volume increases more rapidly than the velocity, as a result of which f_x increases.

Thus, if a gas whose initial state is p_1, v_1 is streamed into a medium whose pressure is $p_2<p_{cr}$ and expands adiabatically, and if it is necessary to attain a velocity c_2 which corresponds to a complete drop in heat content (i_1-i_2), the nozzle

must first narrow and then widen towards the outlet as is shown schematically in Fig. 9-9. The calculation of this type of nozzle boils down to the determination of the cross-sectional area f_{min} by equation 9-22, and $f_2 = G\frac{v_2}{c_2}$ because, theoretically, the final result of the streaming does not depend on the shape of the longitudinal cross-section of the nozzle; it is sufficient for the nozzle first to narrow to f_{min} and then widen to f_2. Different designs for the longitudinal cross-section of the nozzle, provided f_{min} and f_2 are observed, merely change the distribution of pressures throughout the length of the nozzle but do not affect the result of the streaming, i. e., the velocity c_2.

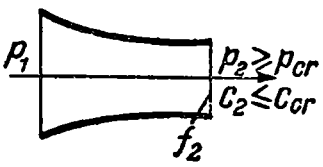


Fig. 9-10

The cylindrical part of the nozzle with a constant cross-section f_2 merely serves the purpose of giving the stream the desired form and does not affect velocity c_2.

If the gas is ejected into a medium with a pressure of p_2 that is equal to or greater than pressure p_{cr}, the nozzle, as can be seen from Fig. 9-8, must narrow towards the outlet and will have the shape shown in Fig. 9-10. The calculation of this type of nozzle requires the determination of the cross-section of the outlet f_2; when $p_2 = p_{cr}$ the cross-section f_2 will be the f_{min} in Fig. 9-8; if, however, p_2 is greater than p_{cr} (Fig. 9-8) the outlet will be greater than f_{min} but will still be the smallest for the given nozzle.

The gas in a nozzle that does not expand towards the outlet will not be able to reduce its pressure to a value lower than p_{cr} and attain a velocity greater than c_{cr}. The leg *bo* of the curve in Fig. 9-7 was obtained on the unfounded assumption that any expansion can be attained in a narrowing nozzle. This assumption is unfounded because the theoretical deductions are not confirmed by practice. If the pressure of the medium, p_2, into which the gas is ejected from a narrowing nozzle, is less than p_{cr} it is obvious that the final result will be the expansion of the gas to pressure p_2, but the expansion shown by the section of the adiabatic *kb* (Fig. 9-8), i. e., from p_{cr} to p_2, does not take place in the nozzle but on the ejection of the stream in different directions as shown in Fig. 9-11, in which case vortical movements are created and there can be no question of a correctly shaped stream such as is essential for the further

use of the kinetic energy of the gas. In the narrowest section of any nozzle, given that p_2 is equal to or less than p_{cr}, the pressure p_{cr} and the velocity c_{cr} are attained, and these values determine the carrying capacity of the nozzle, i. e., its G_{max}. This capacity can only be increased by increasing f_{min}. The widening of the nozzle towards the outlet reduces the outlet pressure p_2 to a value lower than p_{cr} and makes it possible to obtain an outlet velocity c_2 that is greater than c_{cr} without making any change in the weight of the gas expended, G_{max}.

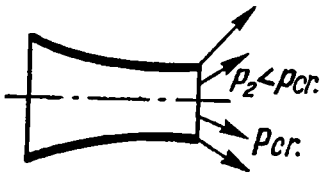


Fig. 9-11

Example 9-1. Air flows into the open from a reservoir with a constant pressure, $p_1=4$ ata and temperature 20° C, through a pipe with a diameter of 10 mm. Determine the hourly expenditure of the air by weight and its final temperature if the outside pressure, $p_2=1$ ata.

For air,

$$p_{cr}=0.528 \quad p_1=0.528\times 4=2.112 \text{ ata} > p_2,$$

so that it flows through a cylindrical pipe with the velocity

$$c_{cr}=3.38\sqrt{p_1 v_1}=3.38\sqrt{RT_1}=3.38\sqrt{29.27\times 293}=313 \text{ m/sec}.$$

The initial specific volume of the air

$$v_1=\frac{RT_1}{p_1}=\frac{29.27\times 293}{40{,}000}=0.215 \text{ cum-kg}$$

and the cross-sectional area of the outlet of the pipe

$$f_{min}=\frac{\pi d^2}{4}=\frac{3.14\times 0.01^2}{4}=0.0000785 \text{ sqm}.$$

In this case, by equation 9-33

$$G=2.15 f_{min}\sqrt{\frac{p_1}{v_1}}=2.15\times 0.0000785\sqrt{\frac{40{,}000}{0.215}}=0.073 \text{ kg/sec}$$

and the hourly expenditure will be

$$G_{hr}=0.073\times 3{,}600=262 \text{ kg/hr}.$$

The final temperature of the air, after expanding adiabatically to pressure $p_2=1$ ata on leaving the pipe, is determined by equation 4-30

$$T_2=T_1\left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}=293\left(\frac{1}{4}\right)^{\frac{0.4}{1.4}}=197^\circ \text{ K}$$

and, therefore,

$$t_2=197-273=-76^\circ \text{ C}.$$

9-4. The Process in a Diffusor. The theoretical streaming process we have examined is one in which the expansion of the gas results in its accelerated movement through a nozzle and in the availability of useful work in the form of the kinetic energy of the stream; this process would be reversible if there were no vortical currents and no friction. If, by expansion *ab* (Fig. 9-8), a velocity of c_2 is attained in a nozzle of cross-section *mkn* and if the gas in the state indicated by point *b* is injected into another nozzle of the same shape but 180° out of phase, i. e., one that changes its longitudinal cross-section according to the curve *nkm*, we shall get a gradual deceleration and consequent increase in pressure along the adiabatic curve *ba*, which will bring the gas to the final state indicated by point *a*. A nozzle of this type, in which increased pressure is obtained by deceleration, is called a *diffusor*; it is widely used in engineering practice, especially in turbocompressors. If the entry velocity of the gas in the diffusor, c_2, is greater than c_{cr}, the cross-section of the diffusor must, as can be seen from Fig. 9-8, first narrow until the velocity is reduced to c_{cr}, determined by the final state of the gas, p_1, v_1, and then widen towards the outlet. If the inlet velocity, c_2, is equal to or less than c_{cr} the diffusor must widen towards the outlet from the very beginning so that the inlet diameter will be the smallest.

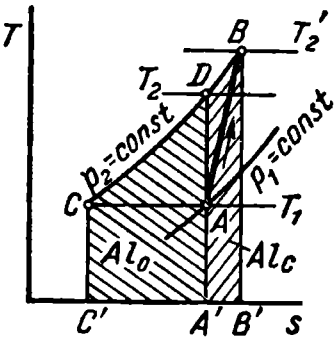


Fig. 9-12

The presence of friction makes a real process in a diffusor irreversible and leads to a loss of work. Fig. 9-12 shows a theoretically irreversible process of the adiabatic compression of a gas in the diffusor according to curve *AB*, as depicted in a coordinate system *Ts* for this process. In complete accordance with what has been said above, in the absence of friction, the expenditure of work in transforming the gas from state *A* to state *D* is

$$Al_0 = i_d - i_a = \text{area } CDA'C',$$

and on the actual process of compression, *AB*, the work expended is

$$Al_0' = i_b - i_a = \text{area } CBB'C'.$$

The extra expenditure of work, i. e., the amount of work lost, is

$$Al_c = Al'_0 - Al_0 = i_b - i_a - i_d \quad i_a = i_b - i_d = \text{area } DBB'A'.$$

This loss is made up of the work of the friction, measured in the usual way as the area $ABB'A'$ below the adiabatic AB, and the additional work of compression measured as area ADB. This additional work is due, as can be seen from Fig. 9-12, to the friction causing a rise in temperature at the end of the process to T'_2 which is greater than the theoretical temperature (T_2) so that in connection with it the specific volume

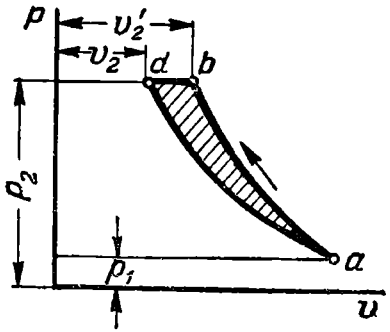


Fig. 9-13

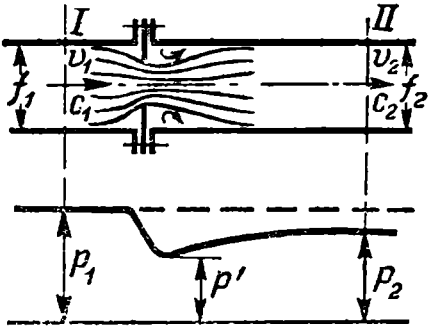


Fig. 9-14

is $v'_2 > v_2$ and the real curve of the compression ab in the system pv (Fig. 9-13) is closer to the vertical than the adiabatic ad; this results in a greater loss of work, one that is equal to the shaded area adb, the equivalent of area ADB in Fig. 9-12.

The losses from friction in a diffusor, therefore, *are greater than the work of the friction.*

9-5. Throttling in a Streaming Process. If there is a sudden narrowing of the channel in the path of the gas or vapour similar to that shown in Fig. 9-14, we know from experience that the pressure, p_2, in the narrow section will be less than the pressure, p_1, prior to the narrowing of the section. This reduction of pressure caused by a resistance in the path of the body is known as throttling.

The loss of pressure ($p_1 - p_2$) is the greater the smaller the diameter of the narrowed section.

If there is no exchange of heat the throttling process is adiabatic; studying the change in the state of the body on passing from section *I* to section *II* and applying to it the

general formula, equation 9-8, we get, after integration, the following

$$i_1 - i_2 = A\,\frac{c_2^2 - c_1^2}{2g} \qquad (9\text{-}24)$$

where i_1 and i_2 are the values of the enthalpy in sections *I* and *II*. It is always possible to select the diameters f_1 and f_2 so that the velocities c_1 and c_2 are equal (see the conditions of continuity); in this case

$$\boxed{i_1 = i_2,} \qquad (9\text{-}25)$$

i. e., *the enthalpy does not change as a result of the throttling* (if $c_1 = c_2$).*

The state of the body changes as can be seen from the following. As the stream passes through the narrowed section its velocity increases so that the pressure drops to p' in the narrowest part of the stream which is a short distance after the throttle; the diameter of the stream at this point is slightly less than that of the throttle. If there is a diffusor it would be possible to convert the additional kinetic energy of the stream into potential energy, i. e., raise the pressure to the initial pressure, p_1; the absence of a diffusor excludes this reversible process. A considerable part of the additional kinetic energy is converted into heat as a result of vortical motions and the collisions taking place beyond the throttle; this heat is imparted to the body, causing an increase in entropy so that the body does not return to its initial state despite the fact that $c_2 = c_1$ and $i_2 = i_1$. The throttling process, therefore, is a typical irreversible process; although it is, in essence, an adiabatic process, there is an increase in entropy. The increase in entropy at equal enthalpy leads to $p_2 < p_1$ and $v_2 > v_1$ as we shall presently see.

For *ideal gases* $di = c_p dt$, at $c_p = \text{const}$; integrating we get

$$i_2 - i_1 = c_p (t_2 - t_1).$$

In a case of throttling $i_2 = i_1$ so that $t_2 = t_1$, i. e., *the temperature of an ideal gas is not changed by throttling*. Therefore, if point *A* shows the state of a gas in the system *Ts*

* Even when the diameter of the pipe is the same before and after the resistance, the change in the velocity of the stream ($c_2 - c_1$) is often so small that it can be ignored and i_1 regarded as being equal to i_2.—*Ed.*

(Fig. 9-15) before throttling, its state after throttling will be represented by point B lying on the same isotherm as point A, but farther to the right since $s_2 > s_1$. According to the fundamental properties of the Ts diagram the pressure $p_2 < p_1$ and the specific volume $v_2 > v_1$ and as a result of equal temperatures, $p_2 v_2 = p_1 v_1$.

It would be incorrect to regard this section of the isotherm AB as the line of the throttling process of the gas because only points A and B give the real states of the gas as those of equilibrium; the intermediate points do not correspond to the real process. In view of the adiabatic nature of the process, the additional velocity at the point of throttling is obtained by a reduction in enthalpy, i. e., it is accompanied by a drop in temperature; after the narrowing of the pipe, as the external kinetic energy is transformed into heat, the temperature rises and at some distance from the throttle, when the stream has regained its correct shape, it reaches the original value. A real process between points A and B, therefore, takes place with t and i variable; at first they decline and then they increase. It is, therefore, not quite correct to define throttling, as is sometimes done, as a process at i=const and, in the case of an ideal gas, at t=const.

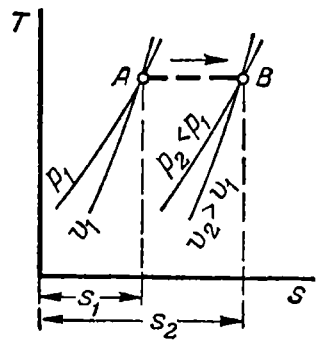


Fig. 9-15

It must be remembered that the relation $i_1 = i_2$ is true only of diameters that are at some distance from the throttle, far enough, that is, for the conditions that obtain before section I to remain unchanged after section II has been passed.

Real gases, that is, those to which the equation $pv = RT$ does not apply, change their temperature slightly during throttling processes. By means of a series of rather complicated processes of differentiation of the equations linking up the values i, s, p and T of the gas we arrive at the following Van der Waals' equation of a relation for the throttling process

$$dT = \frac{\frac{2a}{RT} - b}{c_p} dp,$$

where a and b are, as we know, the constants for the given gas. For throttling processes, dp is always less than zero and the value of c_p is always positive; the sign of dT, therefore, will depend on the sign of the numerator $\left(\frac{2a}{RT}-b\right)$ and there are three possible cases:

1) $dT<0$ at $\frac{2a}{RT}>b$, i. e., $T<\frac{2a}{bR}$;

2) $dT>0$ at $T>\frac{2a}{bR}$;

3) $dT=0$ at $T=\frac{2a}{bR}$.

Thus, we see that, depending on the nature of the gas and the initial temperature, there may be an increase or decrease in temperature as a result of the throttling, or the gas may remain unchanged if the initial temperature is

$$T=\frac{2a}{bR}=T_{\text{inv}}$$

which is the *temperature of inversion.*

For the majority of gases the temperature of inversion is rather high (600° C and higher), with the exception of hydrogen for which $t_{\text{inv}}=-57°$ C. At temperatures higher than T_{inv} the temperature of the gas increases somewhat during throttling and at temperatures lower than T_{inv} it is reduced.

The phenomenon of the reduction in the temperatures of gases during throttling was first established experimentally by Joule and Thomson and is known as the *Joule-Thomson effect*; it is used in refrigerator design. For air, they obtained an average $\Delta t=0.27\,\Delta p$ and for carbon monoxide $\Delta t=1.35\,\Delta p$, i. e., it is five times greater (Δp is in kscm).

The equality, $i_2=i_1$ is only strictly true when $c_2=c_1$; very often, in cases where the velocities are different, however, it may be assumed that the enthalpy does not change as a result of throttling, because the difference

$$i_1-i_2=A\,\frac{c_2^2-c_1^2}{2g}$$

(equation 9-24) is usually insignificant as compared with the value of i_1.

If streaming with throttling were a reversible process a higher velocity would result from the reduced pressure; actu-

ally we have a drop in pressure when $c_2 = c_1$. Throttling is, therefore, accompanied by a loss in available work.

Throttling plays an important part in heat engineering; it occurs when the gas or vapour is passed through a valve, slide or tap, especially when it is not fully opened, and is often a necessary evil that engineers try to reduce. In a number of cases throttling is used for specific purposes; an example is the throttle of an engine, used to reduce the pressure of the gas or vapour in special reducing valves; it is also used to obtain low temperatures in refrigerators and to rarefy gases by multi-stage throttling.

Chapter Ten

THE CYCLES OF GAS TURBINES AND JET ENGINES

10-1. The Cycles of Internal Combustion Turbines. An important shortcoming of internal combustion piston engines is the impossibility of effecting the full adiabatic expansion of the products of combustion inside the cylinder so that internal pressure is reduced to that of the air outside; this involves a loss of work which we measured in Figs. 7-5 and 7-8 as the area DCC_1. Full expansion is, however, attained in engines of the rotary type, in *turbines*, and this greatly increases the thermal efficiency of those engines. Turbines, furthermore, being rotary machines that do not rely on the reciprocating movements of the piston engine, may be designed for work at high speeds, at a greater number of revolutions per minute than a piston engine, and with higher power in a lighter and less cumbersome machine.

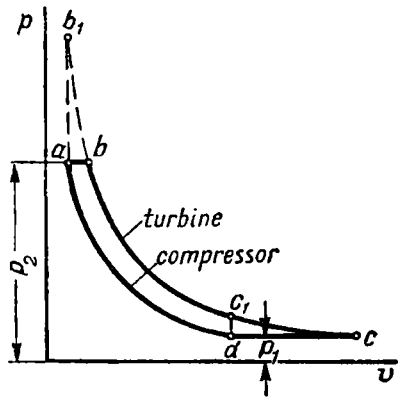


Fig. 10-1

The practical building of turbines, however, involves a number of difficulties both in design and during exploitation; designing engineers are today working on these problems.

The more extensive use of gas turbines in power engineering is an important economic problem that will no doubt be solved in the near future.

Gas turbines work on the two cycles that correspond to the two basic processes in internal combustion engines generally—combustion at constant pressure or at constant vol-

ume. We shall begin by studying the former cycle as depicted in Figs. 10-1 and 10-2 by two isobars and two adiabatic curves. Compression *da* is effected in a special air compressor, combustion *ab* in a combustion chamber, expansion *bc* in the turbine and the cooling process *cd* in the outside air.

Fig. 10-3 is a schematic diagram of a gas turbine. *A* is the rotary compressor supplying compressed air to the combustion chamber *B*; *C* is the oil pump supplying fuel to the same chamber, and *D* is the gas turbine.

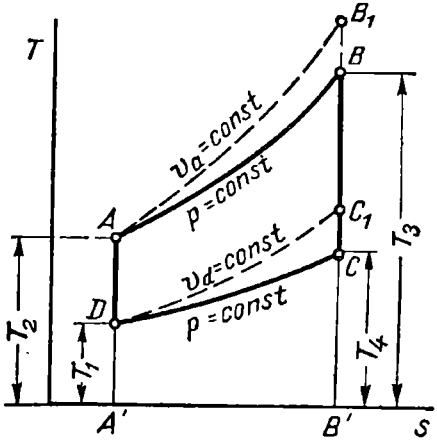


Fig. 10-2

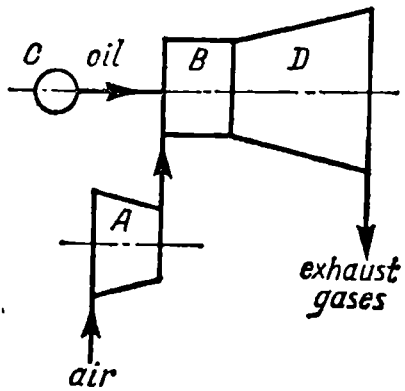


Fig. 10-3

The efficiency of this ideal cycle is

$$\eta_t = 1 - \frac{q_2}{q_1} = 1 - \frac{c_p(T_4 - T_1)}{c_p(T_3 - T_2)} = 1 - \frac{T_4 - T_1}{T_3 - T_2} =$$

$$= 1 - \frac{T_1}{T_2} \times \frac{\frac{T_4}{T_1} - 1}{\frac{T_3}{T_2} - 1}.$$

For the adiabatic curve *da*, by equation 4-30

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}} = \left(\frac{v_d}{v_a}\right)^{k-1}$$

and similarly for adiabatic *bc*

$$\frac{T_3}{T_4} = \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}} = \left(\frac{v_c}{v_b}\right)^{k-1}.$$

It therefore follows that

$$\frac{T_2}{T_1}=\frac{T_3}{T_4} \text{ and } \frac{v_d}{v_a}=\frac{v_c}{v_b}=\varepsilon,$$

i. e., the adiabatic compression and expansion ratios are identical for the given cycle.

Since

$$\frac{T_4}{T_1}=\frac{T_3}{T_2} \text{ and } \frac{T_1}{T_2}=\left(\frac{v_a}{v_d}\right)^{k-1}=\frac{1}{\varepsilon^{k-1}},$$

we get, after the necessary substitutions,

$$\boxed{\eta_t=1-\frac{1}{\varepsilon^{k-1}},} \qquad (10\text{-}1)$$

i. e., the efficiency of the ideal cycle is fully determined by the adiabatic compression or expansion ratio and increases as that ratio. When ε for both systems is identical, the efficiency of the cycle is the same as that of a piston engine with combustion at constant volume (Sec. 7-3) but its highest pressure is lower than that of the piston engine; at constant pressure efficiency is higher than that of a piston engine; for example, at $\varepsilon=16$ the turbine under discussion has an efficiency of 0.6 while for the cycle of the piston engine at $\rho=2.5$, the efficiency is 0.52.

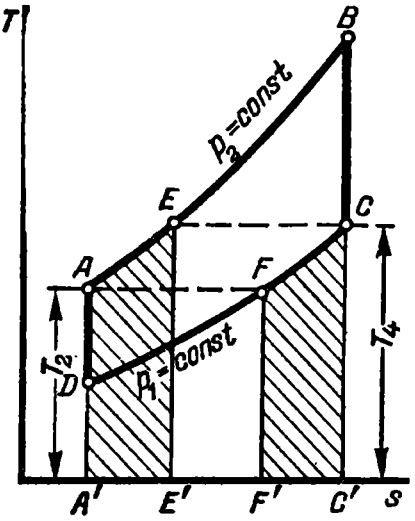


Fig. 10-4

Figs. 10-1 and 10-2 show the cycles ab_1c_1d (corresponding to cycle AB_1C_1D of a piston engine with combustion at v=const) and abc_1d (corresponding to ABC_1D of the piston engine with combustion at constant pressure) and with the same compression ratio ε as the cycle *abcd* of the turbine under discussion; a comparison of these three cycles provides a visual confirmation of the conclusion drawn above.

Since the temperature T_4 of the exhaust gases from the turbine is higher than that of the compressed air, T_2 (Fig. 10-4)

it is advantageous to make partial use of the exhaust gases to raise the temperature of the compressed air theoretically to T_4 at constant pressure p_2 in a special preheater which reduces the temperature of the exhaust gases from T_4 to T_2. In such cases the compressed air enters the combustion chamber in the state indicated by point E at which combustion begins. The amount of heat given off during combustion, q_1= =area $EBC'E'$, is less than in the process AB (in which the air is not preheated) by the area $AEE'A'$=area $FCC'F'$, and since the work of the cycle is identical for both cases and is measured

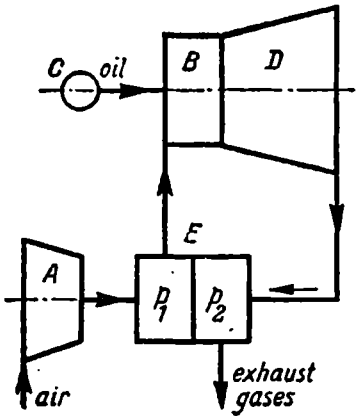


Fig. 10-5

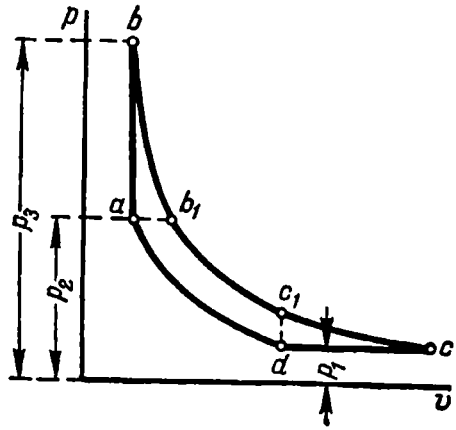


Fig. 10-6

as Al=area $ABCD$, the preheating of the air increases the efficiency of the cycle so that $\eta_t = \frac{Al}{q_1}$. The return of part of the waste heat of the cycle, q_2, to the working body, i. e., to the compressed air, is the *regeneration of heat*, a principle already known to us from Sec. 5-11. We see from this that regeneration makes the cycle more economical.

In Fig. 10-4, DA is again the compression of the air in the compressor, AE is the preheating of the air (regeneration), EB the combustion in the chamber, BC the expansion of the gases in the turbine, CF the cooling of the gases in the regenerator and FD the cooling of the gases in the outside air.

Fig. 10-5 is the schematic diagram of a gas turbine installation with regeneration. It is more complicated than that in Fig. 10-3 having had a regenerator added.

Figs. 10-6 and 10-7 show the turbine cycle with combustion at constant volume; compression *da* takes place in the compressor, combustion *ab* in the combustion chamber, expansion *bc* in the turbine and cooling *cd* in the outside air. The efficiency of the cycle is

$$\eta_t = 1 - \frac{q_2}{q_1} = 1 - \frac{c_p (T_4 - T_1)}{c_v (T_3 - T_2)} = 1 - k \frac{T_4 - T_1}{T_3 - T_2}.$$

The temperatures T_1, T_2 and T_4 may be expressed in terms of T_3: for the process *ab* by equation 4-2

$$\frac{T_3}{T_2} = \frac{p_3}{p_2} = \lambda$$

and, therefore,

$$T_2 = \frac{T_3}{\lambda};$$

and for the adiabatic *da* by equation 4-30:

$$\frac{T_2}{T_1} = \left(\frac{v_d}{v_a}\right)^{k-1} = \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}} = \varepsilon^{k-1}$$

and, therefore,

$$T_1 = \frac{T_2}{\varepsilon^{k-1}} = \frac{T_3}{\lambda \varepsilon^{k-1}};$$

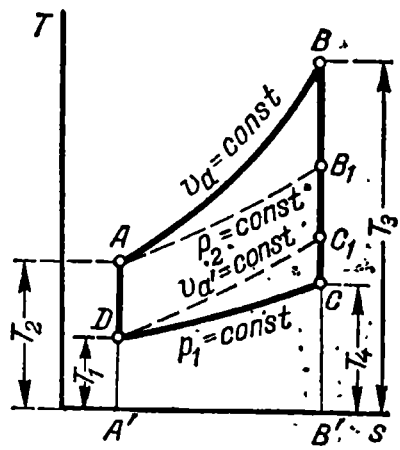


Fig. 10-7

and, lastly, for adiabatic *bc*, by equation 4-30

$$\frac{T_3}{T_4} = \left(\frac{p_3}{p_1}\right)^{\frac{k-1}{k}} = \left(\frac{p_3}{p_2} \times \frac{p_2}{p_1}\right)^{\frac{k-1}{k}} = \lambda^{\frac{k-1}{k}} \varepsilon^{k-1}$$

and, therefore,

$$T_4 = \frac{T_3}{\lambda^{\frac{k-1}{k}} \varepsilon^{k-1}}.$$

After making the necessary substitutions we find that

$$\eta_t = 1 - k \frac{\frac{T_3}{\lambda^{\frac{k-1}{k}} \varepsilon^{k-1}} - \frac{T_3}{\lambda \varepsilon^{k-1}}}{T_3 - \frac{T_3}{\lambda}} = 1 - \frac{k}{\varepsilon^{k-1}} \times \frac{\frac{1}{\lambda^{\frac{k-1}{k}}} - \frac{1}{\lambda}}{1 - \frac{1}{\lambda}},$$

or

$$\eta_t = 1 - \frac{k}{\varepsilon^{k-1}} \times \frac{\lambda^{\frac{1}{k}} - 1}{\lambda - 1}. \qquad (10\text{-}2)$$

Thus, we see that thermal efficiency is determined by the adiabatic compression ratio ε and the increase in pressure during combustion λ, and increases as these values increase; since an increase in λ raises the adiabatic expansion ratio, the efficiency of this cycle, conforming to our previous conclusions, is the higher, the greater the adiabatic compression and expansion ratios. When ε, the compression ratio, is the same in each case, the efficiency of this present cycle is higher than that of a piston engine with combustion at v=const, because in this latter engine $\delta = \varepsilon$, and in our cycle $\delta = \frac{v_c}{v_b} > \varepsilon$. If, for example, $\varepsilon = 8$, the efficiency of the piston engine will be 0.5 and that of the turbine at $\lambda = 2.5$, will be 0.67.

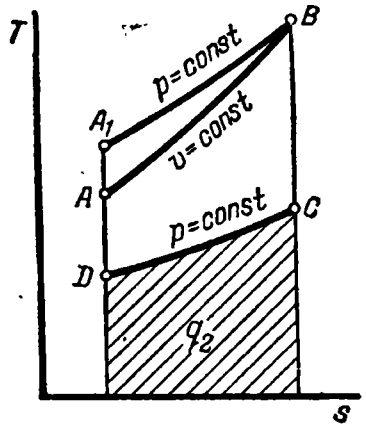


Fig. 10-8

Figs. 10-6 and 10-7 show the cycles abc_1d (corresponding to ABC_1D) of the piston engine with combustion at v=const, and ab_1c_1d (corresponding to AB_1C_1D) of the piston engine with combustion at p=const, ab_1cd (corresponding to AB_1CD) of the gas turbine with combustion at p=const and the cycle under discussion, $abcd$, all with the same compression ratio; a comparison of these diagrams shows that the present cycle has the highest efficiency, followed by abc_1d and ab_1cd that are economically equal and cycle ab_1c_1d with the lowest efficiency.

If we compare the two cycles of the gas turbine at equal maximum pressures and temperatures as is done in Fig. 10-8, it is obvious that the efficiency of cycle A_1BCD with combustion at p = const is higner than that of cycle $ABCD$ with combustion at v=const.

This explains why the majority of modern gas turbines are designed for combustion at constant pressure.

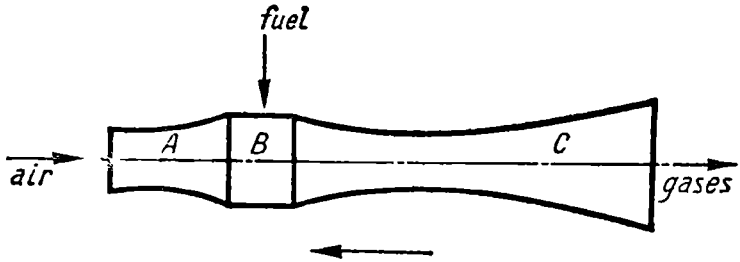


Fig. 10-9

10-2. The Cycles of Jet Engines. *Jet engines*, at present used mainly in aircraft, work according to the following principles.

The stream of gas (the "jet") issuing from the nozzle gives rise to contrary forces along its axis in a direction opposite to that of the stream. If the nozzle is able to move in space these contrary forces will keep it in translational motion; in other words, these forces perform the work of moving the nozzle, and anything connected with it, at a certain velocity.

The cycles employed in the jet engine are the same as those used in the gas turbine, Fig. 10-9 being the greatly simplified schematic diagram of such a jet engine. It consists of the diffusor A, the combustion chamber B and the nozzle C. The high velocity of the air relative to a moving aircraft is sufficient to provide compressed air in the diffusor A without the use of a compressor. Fig. 10-10 is a pv diagram of the jet engine cycle with combustion at constant pressure.

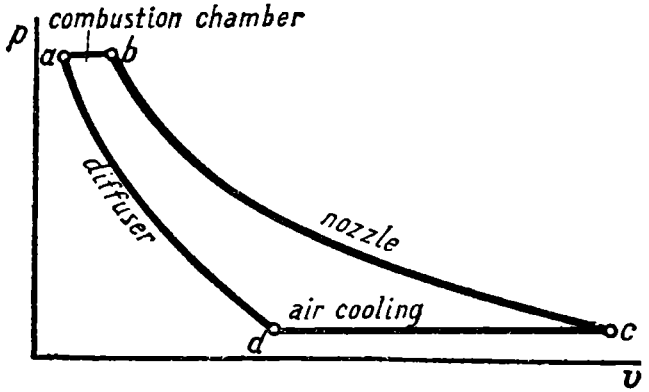


Fig. 10-10

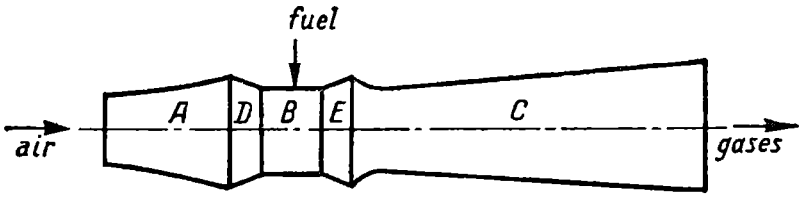


Fig. 10-11

The adiabatic compression ratio, ε, provided by the diffusor is not very great; the thermal efficiency of such engines is, therefore, very low. By raising the degree of compression the thermal efficiency, η_t, can be raised; this is done by placing a turbocompressor behind the diffusor in the front part of the engine and driving it with a small gas turbine; part of the available work of the turbine is used to drive the compressor, the remainder, in the form of exhaust gases at a certain velocity, is passed into the nozzle of the engine where it expands in the usual way providing additional reactive force. A schematic diagram of such a jet engine is given in Fig. 10-11: *A* is the diffusor, *D* the compressor, *B* the combustion chamber, *E* the gas turbine and *C* the nozzle.

Fig. 10-12 is a *pv* diagram of the cycle of this engine: *de* is the compression in the diffusor; *ea*—compression in the compressor; *ab*—the combustion of the fuel; *bf*—expansion in the turbine; *fc*—expansion in the nozzle; area *gaem*—the work of compression in the compressor; area *gbfh*—the work of expansion in the turbine; theoretically these two areas should be equal.

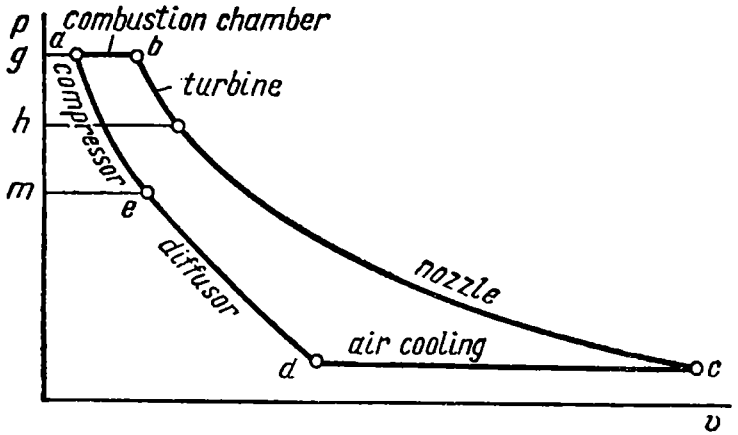


Fig. 10-12

Chapter Eleven

STEAM

11-1. Formation of Vapour at Constant Pressure. Let it be assumed that we have 1 kg of some liquid at 0° C and specific pressure p; let its volume (its specific volume) under these conditions be v_0, the state indicated in the pressure-volume diagram (Fig. 11-1) as point a, whose coordinates are p and v_0'. If this pressure is maintained and heat is imparted to the liquid we know that its temperature will gradually rise, not indefinitely, but up to a certain point, i. e., until it reaches *boiling point* for the given pressure, when its temperature will be t_s. As a rule the volume of the liquid will increase simultaneously from v_0' to v', water being the exception to the rule; water has its greatest density (and, therefore,

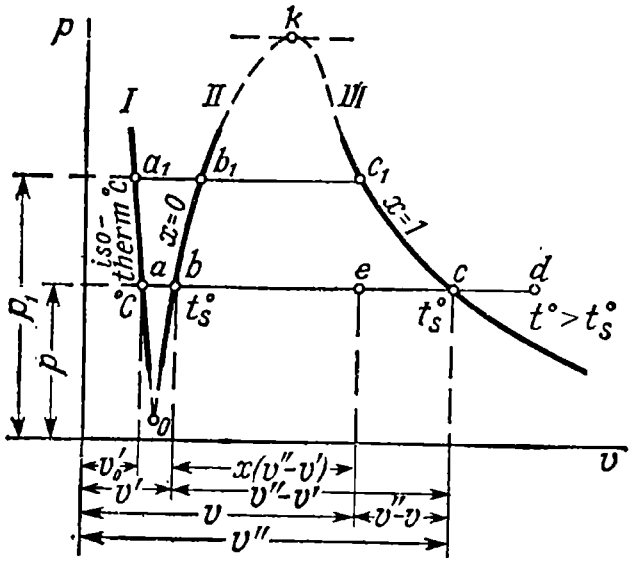


Fig. 11-1

its smallest volume) at 4° C and when heated from zero to 4° C its volume decreases and then, from 4° C to 8° C it again increases and at 8° C has the same volume as at zero. In the *pv* diagram boiling point is indicated by point *b*.

As heat is imparted the liquid boils and is transformed into vapour; if the pressure *p* is kept constant we get a phenomenon common to all liquids—the temperature of the mixture of vapour and liquid remains unchanged at boiling point, t_s, until the entire mixture has vaporised and attained the specific volume v'' which is usually considerably greater than v'. This state is indicated by point *c* in the *pv* diagram (Fig. 11-1).

The section of the isobar *ab* in our diagram represents the heating of the liquid from 0° C to t_s at constant pressure, and the section *bc* represents the process of boiling, or vapour formation at the same pressure and, of course, at the constant temperature of t_s corresponding to that pressure; isobar *bc*, therefore, is also an isotherm.

Vapour in the state indicated by point *c* is known as *dry saturated vapour*; between points *b* and *c* of the isobar there is a mixture of the liquid and dry saturated vapour; if the vapour contains particles of the liquid in suspension (entrained liquid) it will be *wet saturated vapour*.

If further heat is imparted to the dry saturated vapour (point *c*) at the same constant pressure, both the volume and the temperature of the vapour will increase and it will become *superheated vapour*, as for example at point *d*, where the temperature is higher than boiling point at the given pressure; the section *cd*, therefore, is not an isotherm.

The temperature at which a liquid boils is also the temperature of its saturated vapour at the given pressure; we may, therefore, describe it as *vapour in contact and thermal equilibrium with the liquid from which it was formed*. If a saturated vapour is cooled at constant pressure it will gradually return to its liquid state while maintaining the same temperature—i. e., will *condense*; the temperature of the mixture cannot be lowered until all the vapour has become liquid, i. e., the *temperature of the saturated vapour at the given pressure cannot be lowered because it is the lowest temperature of the vapour that is possible at the given pressure.*

By heating dry saturated vapour at constant pressure we may raise its temperature as superheated vapour to any level. This is impossible as long as any particles of the liquid re-

main suspended in the vapour because heat imparted will be used to convert those particles into vapour.

Superheated vapour, therefore, may be described as *vapour at a temperature higher than that of saturated vapour at the same pressure*. Dry saturated vapour is in a state of great instability; the slightest withdrawal of heat at constant pressure results in its partial condensation and the return to its liquid state; if further heat is imparted to it, it becomes superheated vapour.

It must be mentioned that there are cases in which deviations from the above laws are possible—i. e., a liquid may be *heated* to a temperature higher than boiling point (that is, above the temperature of saturated steam at the given pressure) or its vapour may be *cooled* to a temperature lower than boiling point. The first phenomenon sometimes occurs during the slow heating of a liquid that is not in motion and does not contain any admixture of solid or gaseous substances; the second phenomenon may occur when cooling a pure vapour that is also free of foreign matter. Both these states, i. e., heating and cooling above and below boiling point, are unstable.

A liquid turns into vapour at a temperature lower than boiling point for the given pressure if the partial pressure of the vapour over the free surface of the liquid is less than that of the saturated vapour corresponding to the temperature of the liquid. In such cases *evaporation* takes place on the surface of the liquid until the partial pressure of the vapour attains the pressure of saturation.

The formation of vapour at boiling point takes place throughout the entire mass of the liquid but evaporation takes place at lower temperatures and only on the free surface. When a liquid is being heated evaporation always precedes boiling and increases as temperature increases.

Let us return to Fig. 11-1; having found a number of values for v'_0, v' and v'' and plotted the corresponding points a, b, c, a_1, b_1, c_1, etc., on the pv diagram, we get three curves, *I*, *II* and *III* which show the dependence on pressure of: *I*—the specific volume of the liquid at 0° C; *II*—the specific volume of the liquid at boiling point and *III*—the specific volume of the dry saturated vapour. Curve *I* is obviously the isotherm of the liquid at 0° C.

In our further studies we shall confine ourselves mainly to steam, the vapour of H_2O, which is of paramount impor-

tance in modern engineering; for purposes of comparison we shall cite the properties of other vapours and give the data for those of mercury (Hg), sometimes used in turbines, ammonia (NH_3), carbon dioxide (CO_2) and sulphur anhydride (SO_2) which are used in refrigeration techniques.

As we have already said, *there is a definite temperature at which a given liquid boils for every given pressure*; *this also applies to its saturated vapour*; the boiling point of all liquids increases as pressure increases. The pressure and temperature of saturated vapour, therefore, are interdependent; this is expressed in the general case by

$$p = f(t_s)$$

which has been obtained by the adjustment of empirical formulas to the results of experimentation. We shall not give these formulas since they are not used in practice and the corresponding values of p and t_s are given in tables describing saturated vapours. The general character of the interdependence of p and t_s is shown in Fig. 11-2; by comparing the curves in this graph we see that at one and the same pressure different liquids have greatly different boiling points, and, contrariwise, that vastly different pressures of the saturated vapours of different liquids correspond to one definite temperature. At a pressure of 25 ata, for example, water boils at 223° C, SO_2 at 93° C, NH_3 at 57° C, CO_2 at 15° C and mercury at 606° C. At a temperature of 100° C the pressures for saturated vapours are: water 1.033 ata; SO_2 28.63 ata; NH_3 63.9 ata; mercury less than 0.001 ata; the existence of the saturated vapour of CO_2 at this temperature is altogether impossible since it is higher than its "critical" temperature which is $t_{cr} = 31.35°$ C; at 100° C the vapour of carbon dioxide is superheated.

The isotherm $t = 0°$ C intersects all the curves in Fig. 11-2 so that curves *I* and *II* in Fig. 11-1 should also intersect them; the ordinate of point *O* in Fig. 11-1 is also the ordinate of the point of intersection of the vertical and the zero division of the axis of the abscissa (Fig. 11-2) with the corresponding curve $p = f(t_s)$. These ordinates represent, for example, for CO_2, 35.4 ata, for NH_3, 4.32 ata, for SO_2, 1.58 ata and for water, 0.006228 ata.

Let us now determine the general character of curves *I*, *II* and *III* in Fig. 11-1.

Liquids are practically non-compressible; for water at 0° C, for example, the coefficient of compressibility, i. e., the relative reduction in the volume for each increased atmosphere of pressure with the limits of 1 and 200 ata is equal to a mean of $\beta = 0.00005$, so that if the specific volume of water at 0° C and 1 ata equals 0.001 cum-kg, at 200 ata it will be

$$v_0' = 0.001 - 0.00005 \times 200 \times 0.001 = 0.00099 \text{ cum-kg}.$$

The coefficient β decreases as pressure and temperature rise.

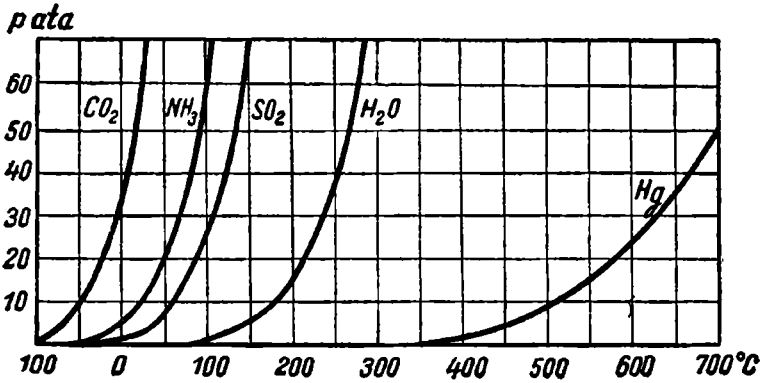


Fig. 11-2

Therefore, although theoretically curve *I* in Fig. 11-1 should approach somewhat towards the axis of the ordinate, in actual fact the dependence of v_0' on p is so slight that in practice it may be considered constant:

for water	$v_0' = 0.001$ cum-kg
" mercury	$v_0' = 0.000073$ "
for ammonia	$v_0' = 0.0016$ cum-kg
" carbon dioxide	$v_0' = 0.0011$ "
" sulphur anhydride	$v_0' = 0.0007$ "

The volume of all liquids increases as temperature rises; each point on curve *II* in Fig. 11-1, whose abscissae give the specific volumes of a boiling liquid, corresponds to a different temperature which rises as the pressure increases. A rise in temperature increases the volume of the liquid and simultaneously an increase in pressure reduces it, but, as we have seen, very slightly. The first effect is considerably greater;

curve *II*, therefore, shifts to the right, away from the axis of the ordinate, and the specific volume of the liquid, v', increases and, consequently, the temperature rises as pressure increases. For example: for water at pressures up to 2 ata $v' \approx \approx 0.001$ cum-kg, and at $p=200$ ata $v'=0.002$ cum-kg. The values of v' are given in tables for saturated vapours.

A large number of experiments have been made by scientists to establish the specific volume of the dry saturated vapours of various liquids; these experiments are extremely difficult because of the difficulty of maintaining the vapour in the unstable state of dry saturation; a very slight heat exchange changes saturated vapour into wet or superheated vapour. It is, therefore, simpler and more reliable to determine the value of v'' mathematically, using experimental data for the other values; this will be dealt with in greater detail in Sec. 11-3.

The specific volume v'' of the dry saturated vapour of all liquids is greater than the specific volume of the liquid v' and decreases as pressure increases while v' increases; as a result, the difference $(v''-v')$, shown in Fig. 11-1 as the section of the horizontal bc, is very great at low pressures and decreases with an increase in pressure.

The dependence of v'' on p in the case of steam is expressed with sufficient accuracy by the empiric equation

$$p^{\frac{15}{16}}v'' = 1.7235, \qquad (11\text{-}1)$$

or

$$pv''^{\frac{16}{15}} = pv''^{1.07} = 1.787, \qquad (11\text{-}2)$$

where p is measured in ata and v'' in cum-kg; this is the equation of curve *III* in Fig. 11-1 and it has the character of a polytrope; since the exponent 1.07 is only slightly greater than unity, the curve is almost an equilateral hyperbola but is a little nearer the vertical.

Equation 11-1 may also be written

$$\gamma'' = \frac{1}{v''} = \frac{p^{\frac{15}{16}}}{1.7235} = 0.58p^{0.9375},$$

where γ'' is the specific weight of dry saturated vapour; by a rough approximation $\gamma'' \approx 0.5p$. In Fig. 11-3 the curves for v'' and γ'' are shown on one graph for steam; the latter passes through the point of origin and is almost a straight line.

The relation between p and v'' also has a hyperbolic character for the vapours of other liquids as is shown in Fig. 11-4 where we have the corresponding curves for SO_2 and NH_3. The values of v'' are given in tables for saturated vapour.

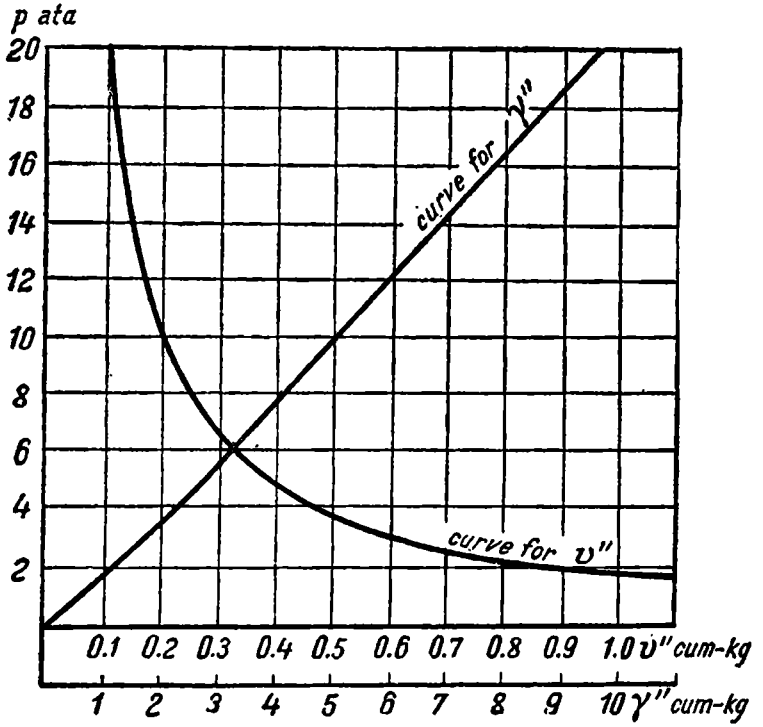


Fig. 11-3

We have established the fact that with an increase in pressure the difference between the specific volume of dry saturated vapour and that of its liquid (v''—v') diminishes; in Fig. 11-1 these differences are shown by the sections bc, b_1c_1, etc. At a certain definite pressure and temperature for the given liquid the difference becomes zero and the curves *II* and *III* meet at point k. This is the *critical* point at which the pressure is p_{cr}, the temperature t_{cr} and the specific volume $v''_{cr} = v'_{cr} = v_{cr}$, values that describe the *critical state* of the vapour (Sec. 1-7); this is obviously a state when the difference between vapour and liquid disappears. The critical temperature is the maximum for the liquid and its saturated vapour; at higher temperatures it may exist only as superheated vapour.

All gases are vapours superheated to a high degree; the higher the temperature of the gas at the given pressure and the lower its critical temperature, the nearer its properties to those of an ideal or perfect gas. In this respect hydrogen, nitrogen, carbon monoxide, air and oxygen come close to perfection as all of them have critical temperatures below 0° C (Sec. 1-7) while carbon dioxide, ammonia and sulphur an-

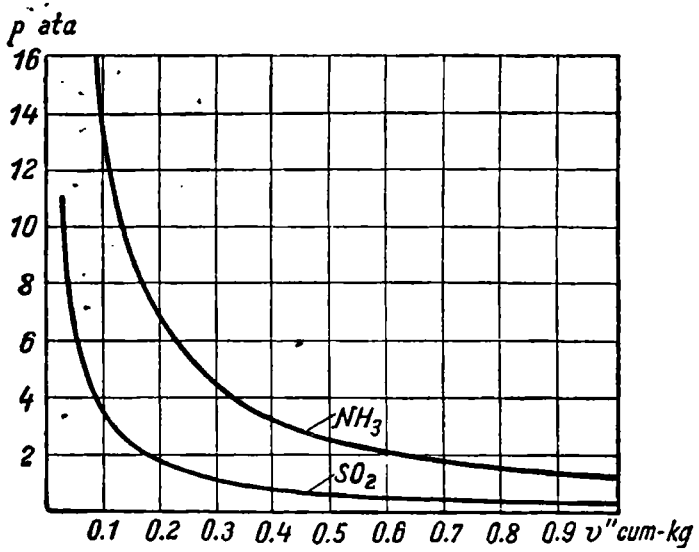


Fig. 11-4

hydride are far from perfect since their critical temperatures are fairly high:

for CO_2, $t_{cr} = 31.35°$ C; for NH_3, $t_{cr} = 132.9°$ C;
for SO_2, $t_{cr} = 156°$ C;
for water $t_{cr} = 374.15°$C and $p_{cr} = 225.65$ ata;
for mercury, $t_{cr} = 1{,}650°$C and $p_{cr} = 3{,}300$ ata.

All points on the horizontal between curves *II* and *III* in Fig. 11-1 correspond to the states of a mixture of the liquid and its saturated vapour; the points on curve *II* determine the state of the liquid at boiling point and those on curve *III* the state of the dry saturated vapour. The points to the left of curve *II* show the liquid at temperatures below boiling point for the given pressure and points to the right of curve *III* correspond to the superheated vapour. Thus curves *II* and *III* in the plane of the *pv* diagram represent the area of

the mixture of liquid and vapour, dividing it from the area of pure liquid (to the left of curve *II*) and from the area of pure superheated vapour (to the right of curve *III*). These curves are therefore called the *threshold curves* of which curve *II* (the water line, indicating boiling liquid) is the *lower* and curve *III* (the saturation line, indicating dry saturated vapour) is the *higher* threshold curve.

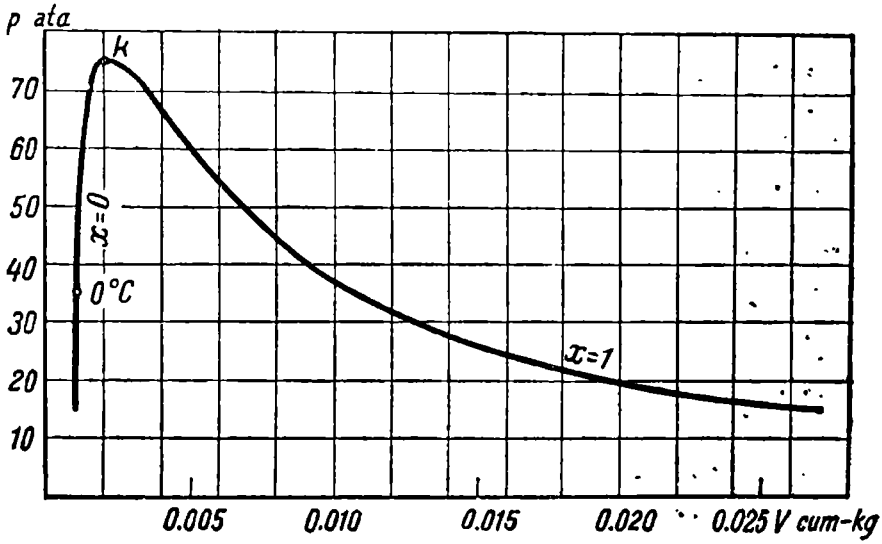


Fig. 11-5

When curves in a *pv* diagram similar to that in Fig. 11-1 are drawn for H_2O, Hg, NH_3 and SO_2 curves *I* and *II* coincide with the axis of the ordinate even when a fairly large scale is used; this is due to the very low values of v'_0 and v' as compared with the volume of the dry saturated vapour (v'') at low and medium pressures so that in practice it is usually only possible to plot the higher threshold curve. For carbon dioxide the curves can be plotted without difficulty because of the much smaller difference in the volumes v' and v''; this has been done in Fig. 11-5 which is drawn to scale with the vertical v'_0 omitted for purposes of clarity; the vertical passes through a point on the lower threshold curve with an ordinate of $p=35.4$ ata, which corresponds to 0° C.

The specific volume of wet vapour. Wet vapour is a mixture of dry saturated vapour and the liquid; its composition is determined from the weight of the vapour, x, contained in 1 kg of the mixture and is called the *degree of dryness* of the

mixture, or by the weight of the liquid in 1 kg of the mixture $(1-x)$ when it is called the *degree of humidity*; in both cases we may speak of the *quality* of the mixture.

The specific volume of the wet vapour, v_x, in the state shown by point e (Fig. 11-1) is the sum of the volumes x kg of dry vapour with a specific volume of v'' and $(1-x)$ kg of liquid with a specific volume of v', i. e.,

$$v_x = xv'' + (1-x)v' = v' + x(v''-v'). \qquad (11\text{-}3)$$

From Fig. 11-1 we see that section $\overline{be} = x(v''-v')$ and since section $\overline{bc} = v''-v'$,

$$x = \frac{\overline{be}}{\overline{bc}}.$$

The same result may be obtained directly from equation 11-3, by which

$$x = \frac{v_x - v'}{v''-v'} = \frac{\overline{be}}{\overline{bc}}.$$

Thus, to determine the quality of the steam at any point e in the pv diagram it is only necessary to plot a horizontal line through the point and measure (in millimetres) the section of it between the given point and the lower threshold curve and between the two threshold curves; the ratio of the first section to the second will give the quality of the steam, x. Should it be necessary to find a point on a given isobar that corresponds to x, it will be sufficient to divide the isobar between the threshold curves in the ratio of $x:1$, i. e., to measure the length of the section in millimetres, multiply it by x and plot the result on the isobar to the right of its point of intersection with the lower threshold curve.

In accordance with the above we may say that the quality of a vapour is

$$1-x = 1 - \frac{v_x - v'}{v''-v'} = \frac{v''-v_x}{v''-v'} = \frac{\overline{ec}}{\overline{bc}}.$$

The quality of the steam, x, may vary from 0 to 1; for the lower threshold curve $x=0$ and for the higher $x=1$.

At pressures lower than 30 ata and $x \geqslant 0.8$ the volume of the water in wet steam is very small as compared with the volume of the steam so that in practice the volume of the water $(1-x)\,v'$ may be ignored and it may be assumed by equa-

tion 11-3 that

$$v_x = xv''. \qquad (11\text{-}4)$$

In reality, even when $p = 30$ ata and $x = 0.8$, we get by equation 11-4 (using the tables)

$$v_x = 0.8 \times 0.06797 = 0.054376 \text{ cum-kg}$$

and by equation 11-3 we get

$$v_x = 0.054376 + 0.2 \times 0.0012142 = 0.054618 \text{ cum-kg}$$

so that the error in the first calculation is a mere 0.44%; at lower pressures and a higher x the error is still smaller. At very high pressures and a high degree of humidity the error is substantial; for example, at $p = 100$ ata and $x = 0.8$ we get by equation 11-4

$$v_x = 0.8 \times 0.01846 = 0.01476 \text{ cum-kg;}$$

and by equation 11-3

$$v_x = 0.01476 + 0.2 \times 0.0014453 = 0.01505 \text{ cum-kg:}$$

here the error is one of 1.96%, i. e., too great for the use of equation 11-4 to be permissible.

11-2. The Heat, Internal Energy, Enthalpy and Entropy of the Liquid. In the general case, when the temperature of 1 kg of liquid is raised to an infinitely small degree, dt, the amount of heat imparted is

$$dq' = c'\,dt = du' + A\,dl = du' + Ap\,dv' \qquad (11\text{-}5)$$

where c'—the weight heat capacity of the liquid;
u'—the internal energy of the liquid;
v'—the specific volume of liquid.

The amount of heat necessary to raise the temperature of a liquid from 0° C to t° C is:

$$q' = \int_0^t c'\,dt = u' - u_0' + A \int_{v_0'}^{v'} p\,dv'.$$

It has been established experimentally that the amount of heat, q', does not depend practically on the nature of the heating process, i. e., in all cases the raising of the temperature from 0 to t °C is almost identical. This is to be explained by the insignificant change in the specific volume v' as a re-

sult of which the second member of the basic equation (the work of expansion) is very small as compared with the first member (the change in internal energy).

If q' does not depend on the nature of the process, then the weight heat capacity of the liquid, $c'=\frac{dq'}{dt}$, does not depend on the heating conditions and can be a function of the temperature alone; it has been established experimentally that it increases as temperature rises, as was the case with gases.

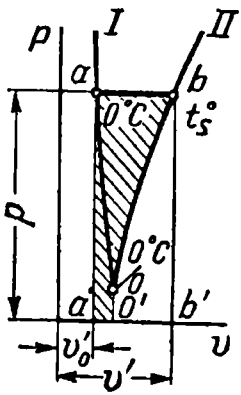


Fig. 11-6

The amount of heat q' is known as the *heat of the liquid* and is, therefore, *the quantity of heat necessary to raise the temperature of 1 kg of liquid from* 0° *to* t °C.

If it be assumed that $v'=\text{const}$, $dv'=0$, $dq'=du'$ and $q'=u'-u_0'$. If q' depends only on temperature then u' is also a function of the temperature alone; assuming conditionally that $u_0'=0$, i. e., calculating the internal energy from 0 °C, we get

$$u'=q',$$

i. e., the internal energy of the liquid is equal to the heat of the liquid.

This is true on the assumption that $v'=v_0'=\text{const}$, and is, therefore, not quite precise; if account be taken of the change in the volume of the liquid, then by equation 11-5, we get

$$\underline{du'=dq'-Ap\,dv'.} \qquad (11\text{-}6)$$

Now let us study the process ab (Fig. 11-6) of the heating of a liquid at constant pressure, p, from 0 °C to boiling point t_s for the given pressure. The basic equation for this process takes the form of:

$$q'=u'+Ap\,(v'-v_0')$$

and, therefore, the exact value of the internal energy of the liquid in the state indicated by point b is

$$\underline{u'=q'-Ap(v'-v_0');} \qquad (11\text{-}7)$$

as an approximation $u'\approx q'$.

For water at $p = 30$ ata ($t_s = 232.76°C$) $q' = 238.9$ Cal per kg, and the work of expansion is

$$Ap(v' - v_0') = \frac{300,000\,(0.0012142 - 0.001)}{427} = 0.15 \text{ Cal/kg},$$

so that

$$u' = 238.9 - 0.15 = 238.75 \text{ Cal/kg}.$$

At $p = 100$ ata ($t_s = 309.53°C$) $q' = 331.66$ Cal/kg so that

$$Ap(v' - v_0') = \frac{1,000,000\,(0.0014453 - 0.001)}{427} = 1.05 \text{ Cal/kg};$$

$$u' = 331.66 - 1.05 = 330.61 \text{ Cal/kg}.$$

The error due to the assumption that $u' = q'$ is 0.06% in the first case and 0.33% in the second, i. e., it is very small.

From Fig. 11-6 we see that, strictly speaking, the amount of heat q' does depend on the conditions of heating; it is, of course, possible to raise the temperature of the liquid from 0° C to t_s, not only by the isobaric process ab, but also by the process ob, during which the pressure gradually increases.

The work l_{ab} is greater than the work l_{ob} by the value of the shaded area $aboo'a'$ and since the internal energy at points o and a is identical *, the change in the internal energy in processes ab and ob is also identical. Therefore, $q'_{ab} > q'_{ob}$ by the amount of heat that is equivalent to the difference in the amounts of work $(l_{ab} - l_{ob})$ which, naturally, is less than Al_{ab}, and, furthermore, we have just established that $Al_{ab} = Ap(v' - v_0')$ is a very small value as compared with q'_{ab}; the difference $(q'_{ab} - q'_{ob})$ is less than this value so that in the case of water, for example, at $p \leqslant 100$ ata it may be ignored and q'_{ab} assumed to be equal to q'_{ob}.

It can be seen from Fig. 11-6 that heating according to threshold curve ob involves the lowest expenditure of heat.

If c'_m is the mean weight heat capacity of the liquid within the limits of 0° and t° C, the heat of the liquid is

$$q' = c'_m t;$$

for water up to 100° C, $c'_m \approx 1$ and, consequently, $q' \approx t$, i. e., the heat of the liquid in Calories is equal to the number of

* Strictly speaking, the internal energy of water at points a and o differs, but the difference is so small that in the majority of cases it may be ignored and it may be assumed that u is a function of the temperature alone.—*Ed.*

degrees of the temperature of the water; at $t=80^\circ$ C, for example, the heat of the liquid (water) is $q'=80$ Cal/kg. As temperature rises c'_m increases, so that at $t=315^\circ$ C, for example, $q'=339$ Cal/kg and at $t=370^\circ$ C, $q'=447$ Cal/kg.

The mean weight heat capacity of mercury

$$c'_m = 0.003 \text{ Cal/kg} \times \text{deg},$$

i. e., at least 30 times less than that of water; the heat of the liquid for mercury is, therefore, insignificant as compared with that of water and within the bounds of the temperatures normally employed, from 185° to 450° C (0.015-4.5 ata), it changes within the limits of 6 to 15 Cal/kg.

For CO_2, NH_3, SO_2 and Hg that solidify at temperatures below zero, the internal energy of the liquid at temperatures below 0° C is negative since we have taken $u'_0=0$ conditionally at 0° C.

By equations 3-35 and 11-7 the enthalpy of the liquid is

$$i' = u' + Apv' = q' - Ap(v' - v'_0) + Apv' = q' + Apv'_0. \quad (11\text{-}8)$$

At low pressures the second member of the equation is very small compared with the first; for water at $p=30$ ata and $t_s=232.76^\circ$C, for example, $q'=238.45$ Cal/kg and

$$Apv'_0 = \frac{300{,}000 \times 0.001}{427} = 0.7 \text{ Cal/kg}$$

so that it may be assumed that

$$i' \approx q',$$

i. e., it may safely be assumed that the enthalpy of the liquid is equal to the heat of the liquid. At high pressures, when precise calculations are needed, the member Apv'_0 cannot be ignored; for water at $p=200$ ata and $t_s=364.08^\circ$ C, $q'=426.6$ Cal/kg, and

$$Apv'_0 = \frac{2{,}000{,}000 \times 0.001}{427} = 4.7 \text{ Cal/kg}.$$

The computation of enthalpy is made from 0° C, assuming that i'_0 at this temperature and at the pressure of saturation (for water $p=0.006228$ ata) is equal to zero although this is not quite exact. We know that at 0° C, $q'=0$, so that by equation 11-8

$$i'_0 = Apv'_0,$$

i. e., the monomial Apv'_0 is nothing more than the enthalpy of the liquid at 0°C, depending on the pressure. For water at the pressure of saturation

$$i'_0 = \frac{62.28 \times 0.001}{427} = 0.000146 \text{ Cal/kg}.$$

In practice it is quite permissible to regard this value as zero.*

We may therefore assume that in the case of water at low pressures

$$i' \approx q' \approx u';$$

in actual fact

$$i' > q' > u'.$$

The entropy of the liquid is described as the increase relative to its state at 0°C and the corresponding saturation pressure (for water $p=0.006228$ ata). At this pressure and temperature the entropy of the liquid is conventionally taken as zero (as at point *o* in Fig. 11-1). As we know, this increase is fully determined by the initial and final states and does not depend on the way in which the change is made from one state to the other since entropy is a function of state. The entropy of the liquid, in its state as at point *b*, therefore, may be described as an increase by process *ob*, knowing that, for reversible processes

$$ds = \frac{dq}{T}.$$

We may write for the process *ob*:

$$s' = \int_{273}^{T_s} \frac{dq'}{T} = \int_{273}^{T_s} \frac{c'\,dT}{T}, \qquad (11\text{-}9)$$

where c' is the weight heat capacity of the liquid. Equation 11-9 is the value of the entropy of the liquid s' at the temperature and pressure of saturation.

If c' be taken as a constant then

$$s' = c' \ln \frac{T_s}{273}.$$

* In compiling the more accurate modern tables for the heat properties of water and steam, the enthalpy of water at 0°C and the pressure of saturation is always taken as zero. The internal energy is defined as $u=i-Apv$. Strictly speaking, therefore, the internal energy of water at the point of origin of the enthalpy calculation is not equal to zero.—*Ed.*

11-3. The Full Heat, Internal Energy, Enthalpy and Entropy of Dry Saturated Vapour. The process *bc*, corresponding to the section of an isobar between the threshold curves in Fig. 11-7, is a process of the formation of vapour in the narrow sense of the word at constant pressure and also at constant temperature; the process is one of the gradual conversion of the liquid into dry saturated steam and of the expansion connected with this conversion.

The amount of heat expended during the process *bc*, i. e., *the amount necessary to convert 1 kg of the liquid heated to boiling point into dry saturated vapour at constant pressure (and temperature)* is known as the *heat of vapour formation and is indicated by the symbol r*. The equation of the first law of thermodynamics takes the following form for the process *bc*

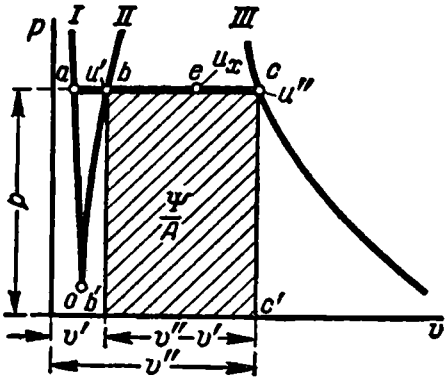


Fig. 11-7

$$r = u'' - u' + Al_{bc} = \\ = u'' - u' + Ap(v'' - v'),$$

where u'' is the internal energy of the dry saturated vapour at point *c*, and u' is the internal energy of the liquid at point *b*.

Thus, a part of the heat of vapour formation, *r*, is expended to change the internal energy, that is, it is expended on the work of dissipation or on overcoming the molecular attraction of the liquid, which is the conversion of liquid into vapour; the remainder being expended on the work of expansion $l_{bc} = p(v'' - v')$, measured as the area *bcc'b'*. There is no change in internal kinetic energy during process *bc* since the temperature is kept constant. If we call the work of dissipation

$$\underline{u'' - u' = \rho} \qquad (11\text{-}10)$$

and the work of expansion

$$\underline{Ap(v'' - v') = \psi} \qquad (11\text{-}11)$$

we may write the equation in the simple form

$$\boxed{r = \rho + \psi.} \qquad (11\text{-}12)$$

The magnitude ρ, since it is the part of the heat of vapour formation that is expended in increasing the internal energy, is called *the internal heat of vapour formation*, and the magnitude ψ, expended on the work of expansion, i. e., on external work, is called *the external heat of vapour formation*.

While the work of dissipation in ideal gases is zero, it is a very significant magnitude in saturated vapour; the greater part of r, the heat of vapour formation, is expended on the work of dissipation ρ, and, in the present case, is accompanied by a change in the physical structure of the body, in the conversion of liquid into vapour; a much smaller part is expended on the work of expansion ψ. For the formation of steam, for example, we get the following figures:

$p=1$	10	50	100	200 ata
$\frac{\rho}{\psi}=12.4$	9.46	7.6	7.0	6.61

The heat of vapour formation r and the internal heat of vapour formation ρ become smaller as the pressure and, consequently, the temperature are raised; the external heat of vapour formation changes to a relatively small degree; at critical temperature (and pressure) $r=0$, $\rho=0$ and $\psi=0$, because under these conditions there is no process of vapour formation and the difference between liquid and vapour disappears.

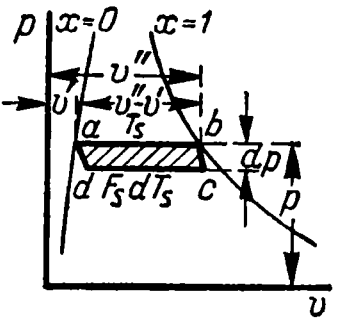


Fig. 11-8

The heat of vapour formation r, the increase in specific volume during the process of vapour formation $(v''-v')$, the pressure p and the temperature of saturation T_s are interconnected in a certain way which is obtained as follows.

Let it be assumed that in the area of saturated vapour we have an elementary Carnot cycle *abcd* (Fig. 11-8) with an infinitely small drop in temperature dT_s, and, therefore, a decrease in pressure dp, and that the initial point, a, of the isothermic expansion lies on the lower threshold curve, with the final point b on the upper curve. The efficiency of the Carnot cycle for 1 kg of the working body is, for the general case,

$$\eta_t = \frac{Al}{q_1} = \frac{T_1 - T_2}{T_1},$$

where l—the work of the cycle, equal to the area of the cycle in the system pv;

q'—the amount of heat imparted during isothermic expansion;

T_1—the absolute temperature of isothermic expansion;

T_2—the absolute temperature of isothermic compression.

In the case under discussion the work of the cycle depicted as the shaded area *abcd*, at an infinitely small dp, will be

$$dl = (v'' - v')\,dp; \quad q_1 = r, \text{ and } T_1 - T_2 = dT_s,$$

so that

$$\frac{A\,(v'' - v')\,dp}{r} = \frac{dT_s}{T_s}$$

or

$$\frac{r}{T_s} = A\,(v'' - v')\,\frac{dp}{dT_s}. \qquad (11\text{-}13)$$

This is known as the *Clapeyron-Clausius* equation.

We have spoken already of the difficulty of determining the specific volume v'' of dry saturated vapour by experimental methods. Equation 11-13 provides a precise method of determining v'' mathematically if the relevant values of v', r and $\frac{dp}{dT_s}$ are known. The values of v' and r may be obtained experimentally by relatively easy and very precise methods as well as the dependence of the pressure on the temperature in the form of the equation $p = f(T_s)$, the first derivative of which is $\frac{dp}{dT_s}$.

The amount of heat that must be expended on the conversion of 1 kg of liquid at 0° C and constant pressure into dry saturated vapour ($x = 1$), i. e., on the process *abc* (Fig. 11-7) is

$$\boxed{\lambda'' = q' + r = q' + \rho + \psi,} \qquad (11\text{-}14)$$

which is *the full heat of the dry saturated vapour*. Fig. 11-9 shows its dependence on temperature for steam; the curves for q', r, ρ and ψ are also shown in this diagram. At 0° C $q' = 0$, $\lambda'' = r = 597.3$ Cal/kg; $\rho = 567.3$ and $\psi = 30$; as temperature and, consequently, pressure rise, λ'' increases slowly as does q', although the latter increases more rapidly than λ'', so that r decreases and ρ with it; the value of ψ increases very

slowly. At 233° C, i.e., p 30 ata, λ'' and ψ have their maximum values, $\lambda''=669$ Cal/kg and $\psi=47$ Cal/kg with $q'=239$, $r=430$ and $\rho=383$. With a further increase in temperature λ'' and ψ, as well as r and ρ, decrease and q' continues to increase; when the body is in the critical state, i. e., when $t_{cr}=374.15°$ and $p_{cr}=225.65$ ata (as at point k), $r=0$, $\rho=0$, $\psi=0$ and $\lambda''=q'=496$ Cal/kg.

For mercury within the limits of 0.015 and 4.5 ata, the heat of vapour formation $r=72$-70 Cal/kg and correspondingly $\lambda''=78$-85 Cal/kg, i. e., much less than the relevant values for water. The magnitude of λ'' for CO_2 and SO_2 is of the same order.

The internal energy of dry saturated vapour according to equation 11-10 is

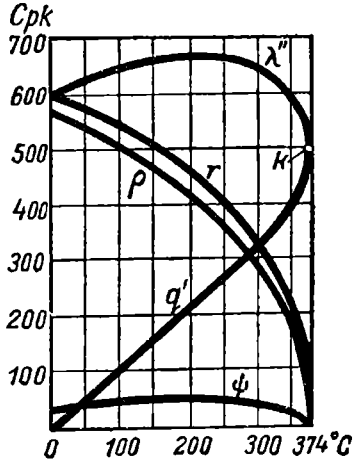


Fig. 11-9

$$\boxed{u''=u'+\rho}, \qquad (11\text{-}15)$$

or, in greater detail, applying equation 11-7

$$u''=q'-Ap(v'-v_0')+\rho; \qquad (11\text{-}16)$$

its approximation is

$$u''\approx q'+\rho. \qquad (11\text{-}17)$$

The enthalpy of dry saturated vapour is obtained by applying equations 11-16, 11-11, 11-12, 11-8 and 11-14:

$$\begin{aligned} i''&=u''+Apv''=q'-Ap(v'-v_0')+\rho+Apv''= \\ &=q'+Ap(v''-v')+\rho+Apv_0'-q'+\psi+\rho+Apv_0'= \\ &=q'+r+Apv_0'=\lambda''+Apv_0'=i'+r. \end{aligned} \qquad (11\text{-}18)$$

If pressures are not very high the monomial Apv_0' may be ignored and it may be assumed that

$$i''=\lambda'',$$

i. e., the enthalpy of dry saturated vapour is approximately equal to its full heat.

The increase in entropy in process *bc* (Fig. 11-7)

$$s'' - s' = \int_b^c \frac{dq}{T_s} = \frac{1}{T_s} \int_b^c dq = \frac{r}{T_s},$$

whence, the entropy of dry saturated vapour is

$$\boxed{s'' = s' + \frac{r}{T_s}.} \qquad (11\text{-}19)$$

11-4. The Full Heat, Internal Energy, Enthalpy and Entropy of Wet Vapour. If r Cal/kg are required to convert 1 kg of liquid at state b into dry saturated vapour, then xr Cal/kg will obviously be required to raise it to state e at the quality of the mixture x (Fig. 11-7), i. e., to convert x kg of liquid into vapour. Therefore, the amount of heat that must be expended on the process ae to convert at constant pressure 1 kg of liquid at 0° C into wet vapour is

$$\underline{\lambda_x = q' + xr,} \qquad (11\text{-}20)$$

a value that is known as the *full heat of wet saturated vapour.*

The work of dissipation, i. e., the increase in the internal energy during process *be* is,

$$u_x - u' = x\rho,$$

so that the internal energy of the wet vapour in the state indicated by point e will be

$$\boxed{u_x = u' + x\rho,} \qquad (11\text{-}21)$$

and in conjunction with equation 11-7

$$\underline{u_x = q' - Ap\,(v' - v'_0) + x\rho;} \qquad (11\text{-}22)$$

and on the assumption that $v' = v'_0 = \text{const}$

$$u_x = q' + x\rho. \qquad (11\text{-}23)$$

The elementary change in the internal energy of wet vapour in the general case by equation 11-6 is

$$du_x = d\,(u' + x\rho) = du' + d(x\rho) = \\ = dq' - Ap\,dv' + d\,(x\rho), \qquad (11\text{-}24)$$

and when v' is constant

$$du_x = dq' + d(x\rho) = d(q' + x\rho).$$

During process *be* the amount of heat xr is imparted at constant pressure p, which goes entirely to increase the heat content; correspondingly the increase in enthalpy in this process is

$$i_x - i' = xr$$

and, consequently, the enthalpy of wet vapour

$$\boxed{i_x = i' + xr.} \qquad (11\text{-}25)$$

And since, by equation 11-8, $i' = q' + Apv'_0$, in conjunction with equation 11-20, we get

$$i_x = q' + xr + Apv'_0 = \lambda_x + Apv'_0. \qquad (11\text{-}26)$$

At low pressures the second member ($Apv'_0 = i'_0$) is very small so that we may assume that

$$i_x = \lambda_x,$$

i. e., a sufficiently close approximation is that the enthalpy of wet vapour is equal to its full heat.

The increase in entropy in the process *be* is

$$s_x - s' = \int_b^e \frac{dq}{T_s} = \frac{1}{T_s}\int_b^e dq = \frac{xr}{T_s}$$

whence, the entropy of wet vapour is

$$\boxed{s_x = s' + \frac{xr}{T_s}.} \qquad (11\text{-}27)$$

11-5. Superheated Vapour. The Equation of State of Superheated Vapour. Its Heat Capacity at Constant Pressure. If heat is imparted to dry saturated vapour at constant pressure its temperature and volume will increase and it will become *superheated* vapour, part of the added heat being used to raise the temperature, part on the work of dissipation, and the remainder to increase the volume, i. e., the external work of expansion.

The properties of superheated vapour differ greatly from those of saturated vapour and approach those of the gases; experiments show that the greater the superheat the more closely its properties approximate those of gases—*superheat* being understood as the *difference in the temperature of the superheated vapour and that of saturated vapour at the same pressure*; as we have already mentioned, the greatly superheated vapours of water and carbon dioxide may be regarded

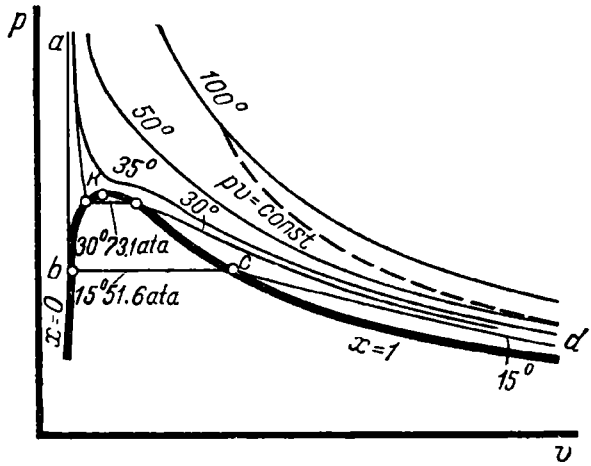


Fig. 11-10

as gases in practice. Since the real gases are actually the superheated vapours of certain liquids they diverge from the laws governing perfect or ideal gases; the less the extent to which they are superheated, the greater the divergence.

The above thesis is excellently illustrated in Fig. 11-10 by a series of isotherms for carbon dioxide (CO_2) in a *pv* diagram. At temperatures below the critical (for CO_2, $t_{cr}=31.35°$ C) the isotherm consists of three parts: the right-hand part, *cd*, is the isotherm of superheated vapour which is closer to the horizontal than the upper threshold curve; the middle line, *bc*, is the isotherm of saturated vapour, a section of horizontal line, and the left-hand part, *ab*, is the isotherm of the liquid which rises so steeply to the left that it is almost vertical. The higher the temperature, the shorter the central, straight-line, part of the isotherm; at critical and higher temperatures this part of the curve disappears altogether. Nevertheless, the isotherm at temperatures slightly above

critical is not a regular curve although it relates exclusively to superheated vapour; in the vicinity of point k there is a small section that is reminiscent of the horizontal part of the isotherm for saturated vapour: such, for example, is the isotherm for $t=35^\circ$ C in Fig. 11-10. As the temperature rises this "step" in the curve shortens until it finally disappears; the isotherm for $t=100^\circ$ C, for example, is a regular hyperbolic curve, more inclined to the horizontal than that of an ideal gas whose equation is $pv=\text{const}$, i. e., it is an equilateral hyperbola. The higher the temperature, the closer the isotherm of superheated steam to an equilateral hyperbola and the closer the properties of the superheated vapour to those of a gas.

The deviation of real gases and superheated vapours from the equation $pv=RT$ is to be explained by the finite volume of the molecules and the existence of attraction between them which is absent in ideal gases. The force of molecular attraction is considerable in liquids so that a substantial part of the heat of vapour formation goes to the work of dissipation. It is only natural that the closer superheated vapour is to the state of saturation the stronger the effect of molecular attraction and the greater the deviation from the properties of an ideal gas.

We see from Fig. 11-10 that any gas or superheated vapour at temperatures below the critical may easily be converted to their liquid state by isothermic compression; carbon dioxide, for example, at 15° C compressed to 51.6 ata becomes liquid carbonic acid in the state indicated by point b. The higher the temperature, the higher the pressure needed to bring about liquefaction; it is 73.1 ata for carbon dioxide at 30° C. Liquefaction is, in general, impossible at temperatures higher than the critical. Thus, the imperative condition for the liquefaction of a gas or vapour is the lowering of its temperature below critical and compression to the pressure of saturation for the given temperature.

Van der Waals' equation shows noticeable deviations from experimental data when applied to superheated vapours; at various times a number of authors have proposed equations connecting the p, v and T of superheated vapours; all of them are based on the equation $pv=RT$ with the addition of other members determined empirically on the basis of experimentation; the majority of these equations have been compiled for superheated steam.

The most precise of a large number of equations for superheated steam is that produced by M. P. Vukalovich jointly with I. I. Novikov in 1939; this equation takes into consideration the phenomenon of associations of molecules (see Sec. 1-7). The equation is necessarily of so complicated a nature that we shall not give it in this book, especially as it is not used in practical calculations.

On the basis of their equation and the differential equations of thermodynamics, Vukalovich and Novikov drew up detailed tables giving the values for v, i and s, which greatly facilitate calculations.

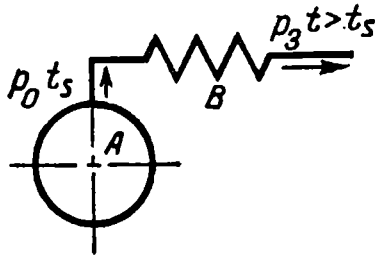


Fig. 11-11

The deviation of superheated vapour from the equation $pv=RT$ is the greater, the lower the temperature T, and, therefore, the less the degree of superheating at the given pressure and the greater the pressure p, because the greater the temperature of saturation the less the degree of superheating at the given temperature T. From the standpoint of the kinetic theory this phenomenon is explained by the fact that a reduction of T and an increase of p decrease the specific volume, i. e., increase the density of the vapour thus increasing molecular attraction and the effect of the volume of the molecules.

Superheated steam in heat installations is usually obtained from dry saturated steam by heating it at constant pressure in a special *superheater*. The design of the superheater is shown schematically in Fig. 11-11. Dry saturated vapour at pressure p and the temperature t_s corresponding to that pressure is generated in the boiler A and passed through the coils of the superheater B which receives its heat from the waste gases of the fire and then passes to the steam pipe for ordinary use. Since the superheater is in constant contact with the boiler the vapour in it, if there is no appreciable resistance, is practically at the same pressure as that in the boiler which is kept constant during operation. Thus, the vapour in the superheater receives heat from the firebox gases at constant pressure and raises its temperature from t_s to t.

The amount of heat required to convert 1 kg of dry saturated vapour at constant pressure into superheated vapour at

temperature t is known as the *superheat*; if we give it the symbol q_s we get the following formula in the usual way

$$q_s = \int_{t_s}^{t} c_p \, dt, \qquad (11\text{-}28)$$

where c_p is the weight heat capacity of superheated vapour at constant pressure.

To determine q_s by equation 11-28 it is necessary to know c_p. It has been found experimentally that the c_p of superheated vapours depends on temperature and pressure. Naturally, the greater part of the investigations have been carried out with steam since it is the vapour that has the greatest importance in heat engineering. Many experiments have been made, beginning from 1906, and the range of temperatures and pressures has gradually been increased. Outstanding among these experiments are those made between 1947 and 1950 at the Dzerzhinsky Heat Engineering Institute by Timrot and Vargaftik. These experiments carried the range of temperatures and pressures to a higher level than ever before, either in the U. S. S. R. or abroad; temperatures up to 600° C and pressures up to 300 ata were used.*

All experiments show that the heat capacity c_p:

(1) *at first rapidly decreases when the temperature is raised at constant pressure from that of saturation t_s, drops to a certain minimum, and then begins slowly to rise,*

(2) *for one and the same temperature it is the higher, the greater the constant pressure and this dependence on pressure is the less, the higher the temperature.*

These facts are clearly illustrated by Fig. 11-12, which is a partial summary of the results of experiments in the form of a series of isobars in a coordinate system $c_p t$. We see from this diagram that c_p depends on pressure to a greater degree the lower the temperature of the vapour, i. e., the closer it is to a state of saturation; as the temperature rises this dependence weakens and at sufficiently high temperatures and, consequently, a high degree of superheating, need not be taken into consideration any more than it is in the gas equations. By a certain degree of approximation the c_p of highly

* Since that time experimental investigations of the properties of water and steam at higher temperatures and pressures have been carried out at the Dzerzhinsky Heat Engineering Institute and other research organisations.—*Ed.*

superheated steam may be taken as a straight-line function of the temperature as can be seen from Fig. 11-12.

The initial points of the isobars are the temperatures and pressures of dry saturated vapour; these points give a curve indicating c''_p, the weight heat capacity of dry saturated vapour at constant pressure which is also the threshold curve ($x=1$) between the areas of superheated vapour (to its right) and saturated vapour (to its left).

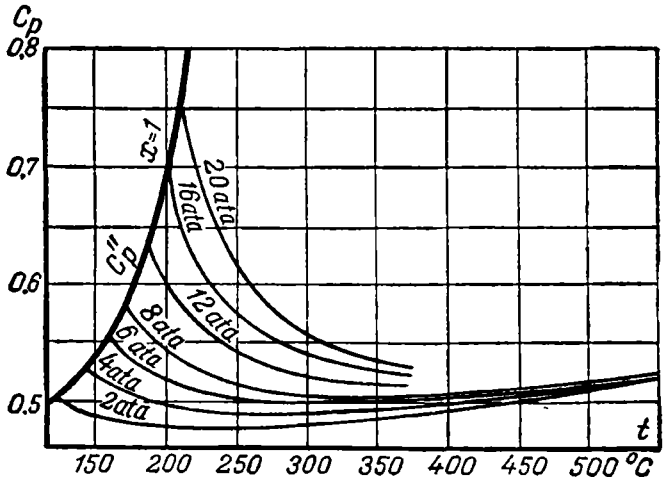


Fig.11-12

The analytical expression of the dependence of c_p on temperature and pressure consists of rather complicated empiric formulas. It would be too tiresome, for practical purposes, to integrate equation 11-28 to determine the superheat q_s owing to the intricate nature of the dependence of heat capacity on temperature. Calculations are greatly simplified (as is the case with gases) by introducing the *mean value of weight heat capacity*, c_{pm}, and by using detailed tables of these values.

If the curve of the true values of c_s is given for a definite pressure, p (Fig. 11-13), the superheat of the vapour, q_s, in the state indicated by point d (i. e., at pressure, p, and temperature, t) will be

$$q_s = \int_{t_s}^{t} c_p dt,$$

and is measured as the shaded area $cdd'c'$ below the section of the isobar cd. Converting this to a rectangle of equal area

$mnd'c'$ with the base $(t-t_s)$, we get as the height of the rectangle the mean value of the weight heat capacity, c_{pm}, in the temperature range t_s-t, as

$$c_{pm}=\frac{q_s}{t-t_s}\ . \qquad (11\text{-}29)$$

We see from Fig. 11-13 that the c_{pm} of superheated vapour is not the arithmetic mean of the extremes. In the appendix there is a table of the values of c_{pm} for superheated steam; using these tables it is quite easy to find the value of the superheat since from equation 11-29

$$q_s=c_{pm}(t-t_s). \qquad (11\text{-}30)$$

If the isobar cd is continued into the area of saturation it changes into a vertical line at the point c (Fig. 11-13) because, as we know, for saturated vapour at p=const and t_s=const, c_p will equal ∞.

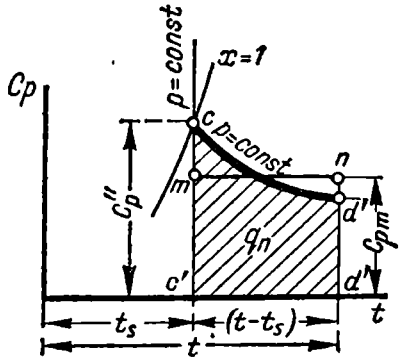


Fig. 11-13

11-6. The Full Heat, Internal Energy, Enthalpy and Entropy of Superheated Vapour. To obtain superheated vapour at a temperature of t from a liquid at 0° C and a constant pressure of p there must be expended on each kilogram of vapour the amount of heat

$$\lambda=\lambda''+q_s=q'+r+c_{pm}(t-t_s), \qquad (11\text{-}31)$$

which is known as the *full heat of the superheated vapour*.

The equation of the first law as applied to the process of superheating cd (in Fig. 11-1) acquires the form

$$q_s=u-u''+Ap(v-v''),$$

whence the internal energy of superheated vapour is

$$u=u''+q_s-Ap(v-v''). \qquad (11\text{-}32)$$

The enthalpy of superheated vapour by equations 3-35 and 11-32 is

$$i=u+Apv=u''+q_s-Ap(v-v'')+Apv=$$
$$=u''+Apv''+q_s=i''+q_s, \qquad (11\text{-}33)$$

which, incidentally, could have been derived directly since the superheat, q_s, imparted to the vapour at constant pressure, is used entirely to increase its enthalpy.
Since $i''=\lambda''+Apv_0'$ (by equation 11-18),

$$i=\lambda''+Apv_0'+q_s=\lambda+Apv_0'\approx\lambda. \qquad (11\text{-}34)$$

The elementary increase in entropy during superheating at constant pressure is

$$ds=\frac{dq}{T}=\frac{c_p dT}{T};$$

its increase during the process cd (Fig. 11-1) of superheating from temperature T_s to T is

$$s-s''=\int_{T_s}^{T}\frac{c_p dT}{T},$$

so that the entropy of superheated vapour at pressure p and temperature T will be

$$s=s''+\int_{T_s}^{T}\frac{c_p dT}{T}, \qquad (11\text{-}35)$$

where s'' is the entropy of dry saturated vapour at the same pressure. Since, in the case of steam, we have analytical dependence of c_p on T, the computation of the integral in the right-hand part of the equation does not involve any difficulty although it is, in general, rather laborious. It is not necessary in practice because the value of s can be found from the tables.

11-7. The Steam Tables. It is obvious that the properties of saturated vapour are much more intricate than those of ideal gases for which any two of the three variables p, v and t, equally determine the third, and, therefore, the state of the gas, since they are interconnected by the simple equation $pv=RT$; any pair of these three variables may be regarded as independent.*

The pressure of saturated vapours is a function of the temperature so that the variables p and t_s do not determine the

* In order to make full use of the most important properties of a gas it is essential to know, furthermore, the dependence of the heat capacity of the given gas on the temperature.—*Ed.*

state; a definite temperature corresponds to a definite pressure, but the specific volume v_x may have any value within the limits v' and v'' depending on the quality of the vapour, x, and the value of v_x is determined by a pair of values p and x or t_s and x in accordance with the relation $v_x=v'+x(v''-v')$, where v' and v'' are functions of either the temperature or the pressure. Thus, for saturated vapour we have a number of analytical relations of a general type: $p=f(t_s)$, $v'=\varphi(t_s)$, $v''=\lambda(p)$ that are, on the whole, rather intricate and differ for different vapours. It would be very laborious to use them for calculations but in practice they are not required since there exist tables for the saturated vapours used in engineering which give the corresponding values of p, t_s, v', v'', γ'', i', i'', r, s' and s''; the specific volume of wet vapour is determined quite easily by the equation $v_x=v'+x(v''-v')\approx xv''$. The variable x is typical of wet vapour and is due to the mixture of liquid and vapour; it is essential to know the composition of the mixture to determine its state.

Naturally, the tables for steam have the greatest practical significance. We give detailed tables for saturated steam as an appendix to this book.

Although there exists an equation for superheated steam based on the relations between p, v and T (the Vukalovich equation) it is, as we have said, too complicated for practical use. Vukalovich compiled superheated steam tables, using his equation, in which the values of v, i and s are given for various temperatures and pressures. The value of the internal energy can be computed from the simple relation $u=i-Apv$. The Vukalovich tables possess a high degree of accuracy.

Example 11-1. Determine the state of steam, i. e., whether it is wet, dry or superheated, given that: (1) $p=8$ ata and $v=0.22$ cum-kg; (2) $p=6$ ata and $t=190°$ C and (3) $p=10$ ata and $t=179°$ C.

1. Since the pressure $p=8$ ata corresponds to a specific volume of dry saturated steam $v''=0.2448$ cum-kg$>v$, it is obvious that steam with a volume of $v=0.22$ is wet; its quality is approximately (equation 11-4)

$$x=\frac{v_x}{v''}=\frac{0.22}{0.2448}=0.897;$$

the exact quality (equation 11-3) is

$$x=\frac{v_x-v'}{v''-v'}=\frac{0.22-0.0011}{0.2448-0.0011}=0.896;$$

we can see from this that the calculation made by the approximated equation is sufficiently accurate. The humidity of the steam is 10.4%.

2. Pressure $p=6$ ata corresponds to the temperature of saturated steam 158.1° C; since the temperature of the given steam $t=190°$ C is higher than the temperature of saturation, the superheat of the steam is $190-158.1=31.9°$ C.

3. Since the pressure $p=10$ ata corresponds to the temperature of saturated steam $t_s=179°$ C, the given steam is saturated; we cannot determine whether it is dry or wet because the pair of variables p and t_s do not determine the state of saturated steam.

Example 11-2. Determine the state of steam at a pressure of 10 ata if 640 Cal/kg have been expended to obtain it at constant pressure from water at 0° C.

Knowing that the enthalpy $i=640$ Cal kg and obtaining the value of i'' for saturated steam at 10 ata as 663.3 Cal kg from the tables, we conclude that the given steam is wet because $i<i''$. Determining the quality of the steam by equation 11-25 we get:

$$i_x=i'+xr$$

so that

$$x=\frac{i_x-i'}{r}=\frac{640-181.3}{483.1}=\frac{458.7}{483.1}=0.95.$$

Example 11-3. A reservoir of 85 litres volume contains 0.1 kg of water and 0.7 kg of dry steam. What is the pressure in the reservoir?

The specific volume of the mixture is

$$v_x=\frac{0.085}{0.1+0.7}=\frac{0.085}{0.8}=0.10625 \text{ cum-kg.}$$

Its quality is

$$x=\frac{0.7}{0.8}=0.875;$$

in this case, by equation 11-4

$$v''=\frac{v_x}{x}=\frac{0.10625}{0.875}=0.1215 \text{ cum-kg.}$$

By interpolation we find the pressure corresponding to this specific volume of dry saturated steam; it is

$$p=16+\frac{1}{0.1261-0.1189}(0.1261-0.1215)=16.65 \text{ ata.}$$

Example 11-4. With the temperature of the feed-water at 40° C, 1 kg of coal burnt in the boiler produces 8 kg of dry saturated steam at a pressure of 12 ata. How many kilograms of steam would 1 kg of the same coal produce at a pressure of 20 ata with feed-water at a temperature of 10° C?

The amount of heat expended on obtaining 8 kg of steam at 12 ata with p=const,

$$Q=G_{12}(i''_{12}-i'_{40})=8(664.9-40)=5{,}000 \text{ Cal;}$$

to obtain 1 kg of dry saturated steam at a pressure of 20 ata, there must be expended

$$q = i''_{20} - i'_{10} = 668.5 - 10 = 658.5 \text{ Cal/kg};$$

therefore, for the expenditure of Q amount of heat we may obtain

$$G_{20} = \frac{Q}{q} = \frac{5{,}000}{658.5} = 7.6 \text{ kg}$$

of steam.

Example 11-5. Determine the weight and enthalpy of 0.6 cum of steam with 20% humidity at a pressure of 4 ata.

The specific volume of the steam by equation 11-4 is

$$v_x = xv'' = (1 - 0.2) \times 0.4709 = 0.37672 \text{ cum-kg}$$

and the weight

$$G = \frac{V}{v} = \frac{0.6}{0.37672} = 1.59 \text{ kg}.$$

The enthalpy of the steam (applying equation 11-25) is

$$I_x = Gi_x = G(i' + xr) = 1.59 (143.7 + 0.8 \times 510.2) = 876 \text{ Cal}.$$

11-8. The *Ts* Diagram for Steam. Steam processes, like gas processes, are described graphically by both the *pv* and *Ts* diagrams; the latter is very widely used and is valuable because the area below the curve of a reversible process gives the amount of heat imparted to the body and the reversible adiabatic process is shown by a vertical line (s=const). Since every point in either system of coordinates describes the state of the body, each point in one diagram corresponds, generally speaking, to a certain definite point in the other. By transferring, point by point, the lower threshold curve (x=0) from the system *pv* to the *Ts* diagram we get the corresponding curve *OB* (Fig. 11-14 and 11-15). Since we have taken the entropy of the liquid in the state indicated by point *O* to be zero, the zero point corresponding to point *O* will lie on the axis of the ordinate at 273° above absolute zero; the abscissae of the points of the curve x=0 will, therefore, be the values of the entropy of the liquid s'.

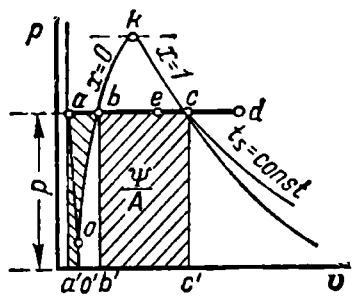


Fig. 11-14

Similarly, the upper threshold curve (x=1) is plotted on the *Ts* diagram and its abscissae indicate the values of the

entropy of dry saturated steam s''. Thus, the section OB of the lower threshold curve corresponds strictly to section ob of the similar curve in the system pv and indicates the process of heating the water from 0°C to boiling point at gradually rising pressure as can be seen from Fig. 11-4. Since we have decided that in all cases a uniform amount of heat

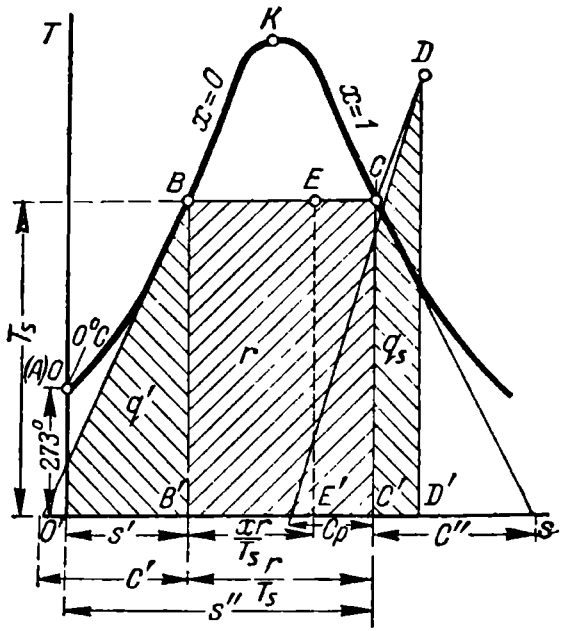


Fig. 11-15

will be expended in raising the temperature of water from 0 to t°C (Sec. 11-2), i. e., the amount of heat, q', the area $OBB'O'$ in the Ts diagram, by its known specifics, will give us the value of q' on a certain scale. The process of steam formation at constant pressure and temperature, bc, corresponds to the section of the horizontal BC in the Ts diagram between the threshold curves, the latter meeting at point K where they touch the horizontal tangent to the curve at this point, indicating the critical state of the body. In both the pv system and the Ts (temperature-entropy) system, points on the horizontal line between the threshold curves correspond to wet steam; points on the curve $x=0$ determine the state of the water at the temperature of boiling and points on the curve $x=1$ show the state of dry saturated

steam; points to the right of this curve indicate superheated steam.

From Fig. 11-15 we find that

$$\frac{\overline{BE}}{\overline{BC}}=\frac{\frac{xr}{T_s}}{\frac{r}{T_s}}=x=\frac{\overline{be}}{\overline{bc}},$$

i. e., the points in the area of saturation that correspond to each other divide the horizontal lines between the threshold curves in the *pv* and *Ts* systems in like proportion.

During the formation of steam, process *bc*, the heat of steam formation, *r*, is expended, and during the process *be*, the heat expended is *xr*, so that the area $BCC'B'=r$ and area $BEE'B'=xr$ which follows naturally from Fig. 11-15, because

$$\text{area } BCC'B'=\frac{r}{T_s}\times T_s=r \text{ and area } BEE'B'=\frac{xr}{T_s}\times T_s=xr.$$

Since area *bcc'b'* in Fig. 11-14 gives the external heat of steam formation ψ in units of work, the internal heat of steam formation ρ is determined as the difference $\rho=r-\psi$. Further, in the *Ts* system we have

$$\text{area } OBEE'O'=\text{area } OBB'O'+\text{area } BEE'B'=q'+xr=\lambda_x;$$
$$\text{area } OBCC'O'=\text{area } OBB'O'+\text{area } BCC'B'=q'+r=\lambda''.$$

The subtangent to the lower threshold curve gives the weight heat capacity of the water, *c'*, and the subtangent of the upper curve ($x=1$) gives the heat capacity of dry saturated steam *c''* during the change in its state according to the threshold curve, i. e., retaining the dry saturation. We see that heat capacity *c''* is negative; to lower the temperature of saturated steam and keep it dry, heat must be imparted to it.

This is true of a number of vapours in addition to that of water, but there are some that have a positive heat capacity *c''*, for example that of diphenyl $(C_6H_5)_2$ whose threshold curves are drawn to scale in Fig. 11-16.

In making our deductions we assumed that the heat of the liquid, *q'*, is expended in raising the temperature from 0°C to boiling point t_s for the given pressure, irrespective of the conditions of heating and that it is, in particular, identical for the processes *ob* and *ab* (Fig. 11-14). On this

assumption, point a obviously corresponds to point O in the Ts diagram, the section of the isobar ab corresponds to the section of the threshold curve OB, the isotherm of the liquid at 0°C merges with the threshold curve at point O (which is also A) and the curve $x=0$ itself corresponds to the entire area of the liquid of the pv diagram. Strictly speaking, this is not quite accurate as we have said in Sec. 11-2; the amount of heat expended on the isobaric process ab is greater by the area $aboo'a'$ than that expended on the process ob on the lower threshold curve. OB, therefore, is not an isobar and the isobar AB should incline more to the horizontal than OB as is shown in Fig. 11-17. Since the tables for saturated steam are compiled on the basis of the value of the heat q' with heating at constant pressure, the area $OBB'O'$ is less than q' (depicted by the area $ABB'A'$) by the value of the shaded area in Fig. 11-17, which, of course, is the equivalent of area $aboo'a'$ in Fig. 11-14.

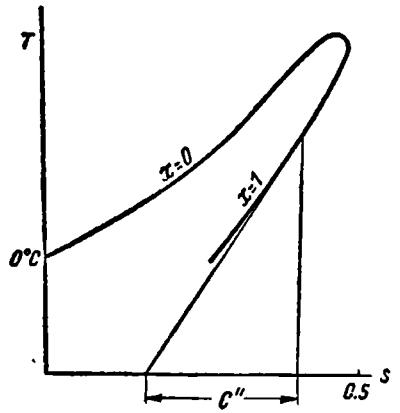


Fig. 11-16

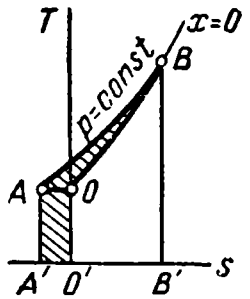


Fig. 11-17

At temperatures and pressures greatly below the critical, the isobars of the liquid practically merge with the lower threshold curve so that it is quite permissible to consider area $OBB'O'$ equal to the heat of the liquid q'.

It will be a sufficiently accurate approximation, at temperatures and pressures that are noticeably below critical, to assume that area $OBB'O'$ (Fig. 11-15) is equal to the enthalpy of the liquid, i', and, therefore, that area $OBEE'O'=ix$ and area $OBCC'O'=i''$; the inaccuracy resulting from this is greater by the value of Apv_0' than that of the assumption that area $OBB'O'=q'$. Actually the corresponding

heat content is greater by the value represented by the shaded area in Fig. 11-17, plus Apv'_0.

In the area of saturation the isobar and isotherm coincide since they are horizontal straight lines in the *Ts* and *pv* systems; as they enter the area of superheat they separate—in the *pv* diagram the isotherm moves downward from the isobar and in the *Ts* diagram the isobar moves upward from the isotherm; their relative positions are similar in both graphical systems, i. e., the isobar of superheated steam is above its isotherm. It is natural that the isobar of superheated steam should be of the same character as that of a gas, i. e., it is a concave curve that rises from left to right. The subtangent of the isobar gives the true value of the heat capacity c_p for the given pressure and temperature.

Equation 11-35 is obviously that of the isobar of superheated steam at p=const in the system *Ts*; since c_p depends on pressure every isobar of superheated steam will be an independent curve which must be plotted in the diagram point by point; in the case of gases, where c_p is independent of pressure, the isobars are like curves, spaced along a horizontal line.

The area *CDD'C'* represents the superheat q_s, and the area *OBCDD'O'* the enthalpy of the superheated steam in the state represented by point *D*, and also the full heat of the steam λ.

The study of steam processes and the calculations connected with them are greatly simplified by the use of detailed *Ts* diagrams in which both threshold curves are plotted and in which there is a network of isobars, isochors and constant-quality curves (x=const) such as that shown in simplified form for steam in Fig. 11-18. The part of the diagram below 0°C is usually not plotted as it has no practical significance; this makes it possible to increase the scale of the axis of the ordinate and include greater detail in the diagram. The constant quality curve is obtained by dividing the horizontal sections between the threshold curves into an equal number of parts and joining up the points of the division. In calculating the area representing the amount of heat below the curve of the process the additional area of the rectangle below the axis of the abscissa must be taken into consideration because the real axis of the entropy is 273°C lower. The isochors in the sphere of saturation are concave curves; they have the same shape in the area of

superheat as the isobars but are somewhat closer to the vertical like those of the gases.

A diagram composed of a detailed network of isobars, isochors and constant-quality curves makes it easy to find points corresponding to a definite state, or, on the contrary,

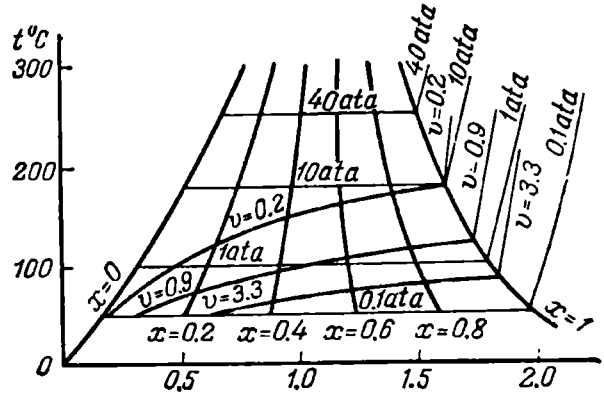


Fig. 11-18

to find the parameters of a given point. Since the engineer mostly has to deal with superheated steam or slightly humid steam, he may compile his diagram from the right-hand part of the system only, thus being able to increase the scale of the axis of the abscissa which makes the diagram easier to work with and the calculations more precise.

11-9. The *is* Diagram for Steam. The heat diagram in the system *is*, in which the abscissae are entropy values as in the system *Ts*, and the ordinates enthalpy (*i*) values, is invaluable in calculating steam processes. To construct the diagram, first plot the threshold curves from the tables (Fig. 11-19). The coordinates of the points on the lower threshold curve ($x=0$) are the values of i' and s' and those of the upper curve are the values of i'' and s''; in conformity with this the vertical distance between the points B and C, common to both curves (i. e., points at the same pressure and temperature), is equal to the heat of steam formation r, and the horizontal distance is equal to $\frac{r}{T_s}$. If we connect B and C by a straight line we obtain the isobar of saturated steam which is also the isotherm, as can easily be proved. According to

equations 11-25 and 11-27, for steam

$$i_x = i' + xr \text{ and } s_x = s' + \frac{xr}{T_s};$$

substituting $xr = i_x - i'$ from the first equation in the second we get

$$s_x = s' + \frac{i_x - i'}{T_s}$$

and at p=const the values of T_s, s' and i' are also constant, so that the last equation is a first-degree equation with the

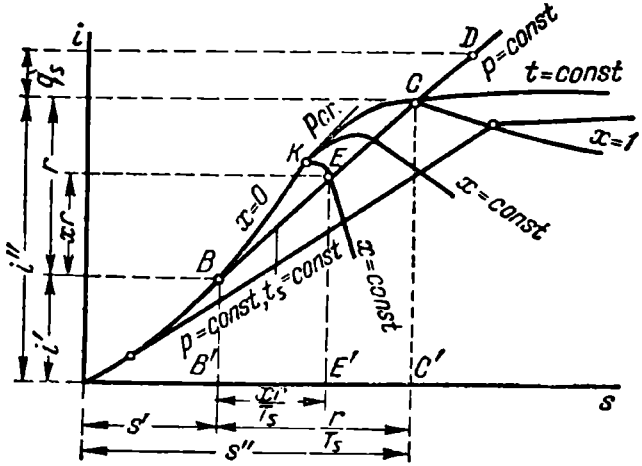


Fig. 11-19

variables s_x, and i_x, i. e., a straight-line equation in the system *is*. From Fig. 11-19 we get

$$\frac{\overline{BE}}{\overline{BC}} = \frac{\overline{B'E'}}{\overline{B'C'}} = \frac{\frac{xr}{T_s}}{\frac{r}{T_s}} = x,$$

i. e., in the *is* graph, in exactly the same way as in the *Ts* and *pv* graphs, the quality of the saturated steam, x, is determined by the ratio of the section of the isobar between the given point E and the lower threshold curve to the section of the isobar between the threshold curves.

In conformity with this, the curves of constant quality are plotted in the same way as in the *Ts* diagram by subdividing the sections of the isobars between the threshold

curves into an equal number of parts and joining the points of similar subdivisions.

The isobars and the isotherm, exactly in the same way as in the *Ts* and *pv* diagrams, coincide in the area of saturated steam and diverge as they enter the area of superheated steam where they become curves, the isobar again falling above the isotherm.

The isobar of superheated steam is concave and rises from left to right and is somewhat closer to the vertical than the straight-line isobar of saturated steam. The isotherm of superheated steam also rises from left to right but is much flatter; the flattening of the curve continues as it gets farther away from the threshold curve $x=1$ and approaches the horizontal asymptotically, the curve being convex. The shape of the isotherm is a perfectly natural one because the farther superheated steam departs from the area of saturation, the closer its properties approximate those of a gas, and for an ideal gas, as we know, when $t=\text{const}$, i is also constant. The heat of superheating, q_s, is represented by the difference in the ordinates of point D of superheated steam and point C of dry saturated steam at the same pressure.

A reversible adiabatic process is represented in the system *is* in the same way as in the system *Ts*, by a vertical straight line ($s=\text{const}$); the quantity of heat imparted to the steam during the isobaric process is represented by the difference in the ordinates of the initial and final points of the process. These properties of the *is* diagram have made its use for practical purposes very widespread. In the USSR today it is used almost universally because, apart from what has already been said, this diagram has other valuable uses that we shall deal with later.

For practical purposes the *is* diagram is not plotted for the entire area of saturation, but only for that part in the neighbourhood of the upper threshold curve so that a bigger scale can be used and a detailed network of isobars, isochors, isotherms and constant-quality curves plotted. A diagram of this type for steam, compiled by Prof. Vukalovich, is given in the appendix.

Chapter Twelve

STEAM PROCESSES

12-1. The Isochoric Process. In the calculation of steam processes there are three possible cases:

(a) the entire process takes place in the area of saturation;

(b) the entire process takes place in the area of superheating;

(c) the process takes place partly in each area.

The simplest and most useful graphical method of calculation is by means of a detailed *is* diagram. If no such diagram is available recourse must be made to analytical methods, using the tables and applying the necessary formulas. If the graphical method is used the nature of the calculation will be the same for all three of the above cases; an analytical calculation will depend on the area in which the process takes place because there are different basic relations for saturated and superheated steam and the tables for the two types of steam differ.

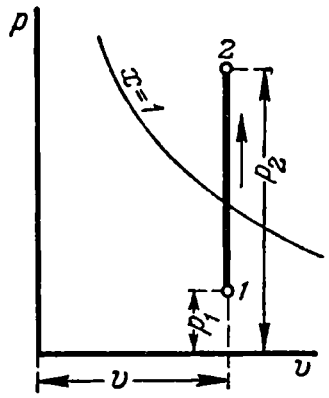


Fig. 12-1

Figs. 12-1, 12-2 and 12-3 represent an isochoric process (for the most general case, "c") shown in *pv*, *Ts*, and *is* diagrams.

Irrespective of the area in which points *1* and *2* lie, $l=0$ for the isochoric process since the amount of heat, q, is equal to

$$q = u_2 - u_1 = i_2 - Ap_2v - (i_1 - Ap_1v) = \\ = i_2 - i_1 - Av\,(p_2 - p_1), \qquad (12\text{-}1)$$

where u_1 and u_2 are the values of internal energy; and p_1 and p_2 are the initial and final pressures.

When the graphical method is used we get the values of i_1, i_2, p_1, p_2 and v directly from the is diagram and substitute them for the symbols in equation 12-1.

In the case of an analytical calculation the value of the enthalpy is determined by equation 11-25:

$$i_x = i' + xr,$$

the values of i' and r being taken from the saturated steam tables for the given pressure; the equation for the quality

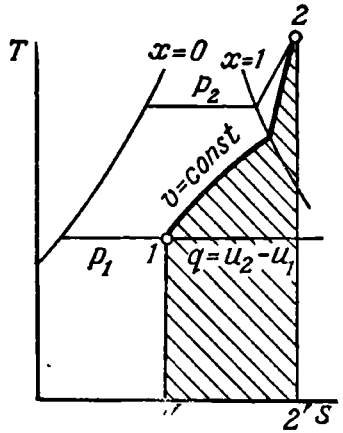


Fig. 12-2

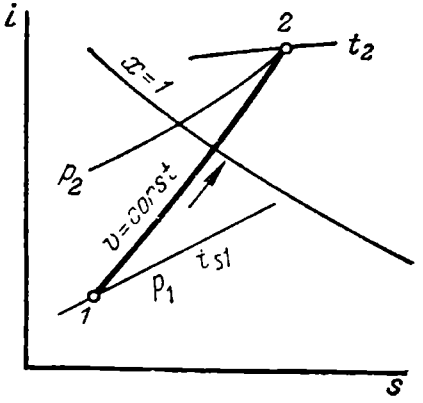


Fig. 12-3

of the steam is $x=\frac{v_x}{v''}$, v'' also obtained from the saturated steam tables. The enthalpy of saturated steam, i, is taken for the corresponding p and t, or p and v, or v and t.

If the process takes place entirely in the area of superheating it can be simply and easily calculated without the is diagram, using tables only; this applies not only to an isochoric process but to any process for superheated steam, as we shall show by the use of concrete examples.

In the pv diagram the process is represented by a section of a vertical line (Fig. 12-1) and in the Ts diagram (Fig. 12-2) it is a curve, convex in the area of saturation and concave in the area of superheat; area 1-2-2'-1' shows the quantity of heat $q=u_2-u_1$. In the is system (Fig. 12-3) the isochor in the saturation area is almost a straight line and in the superheat area it is more curved and slightly concave. In both areas the isochors are somewhat closer to the vertical than

isobars passing through the same points. The increase in internal energy during heating is seen as an increase in temperature, on the one hand, and in the work of dissipation, on the other. The diagrams show clearly that by heating wet steam at constant volume it can be converted in its entirety into dry saturated and superheated steam; it is also obvious that by cooling at constant volume the whole of the steam cannot be converted into liquid because the isochor in the *pv* system and, consequently, in the *Ts* system does not cross the water threshold line which in Fig. 12-1 merges with the axis of the ordinate.

Example 12-1. A boiler contains 7 cum of water and 5 cum of dry steam at a pressure of 4 ata. How long will it take to raise the pressure to 16 ata with closed cocks if the fire gives the boiler 4,200 Cal p. m.?

The initial weight of the water in the boiler

$$G_w = \frac{V_w}{v_1'} = \frac{7}{0.0010829} = 6{,}460 \text{ kg}$$

and the corresponding weight of the steam

$$G_s = \frac{V_s}{v_1''} = \frac{5}{0.4709} = 10.6 \text{ kg};$$

the constant weight of the mixture, therefore,

$$G = G_w + G_s = 6{,}460 + 10.6 = 6{,}470.6 \text{ kg}.$$

The initial quality of the mixture

$$x_1 = \frac{G_s}{G} = \frac{10.6}{6{,}470.6} = 0.00164$$

and its constant specific volume

$$v_x = \frac{V}{G} = \frac{7+5}{6{,}470.6} = \frac{12}{6{,}470.6} = 0.001855 \text{ cum-kg}.$$

The final quality of the steam is obtained from equation 11-3

$$v_x = v_2' + x_2 (v_2'' - v_2')$$

and is equal to:

$$x_2 = \frac{v_x - v_2'}{v_2'' - v_2'} = \frac{0.001855 - 0.0011572}{0.1261 - 0.0011572} = \frac{0.000698}{0.12495} = 0{,}00558.$$

The value of the enthalpy by equation 11-25

$$i_{x_1} = 143.7 + 0.00164 \times 510.2 = 144.536 \text{ Cal/kg};$$
$$i_{x_2} = 204 + 0.00558 \times 463.1 = 206.58 \text{ Cal/kg};$$

by equation 12-1

$$q = 206.58 - 144.536 - \frac{0.001855\,(160{,}000 - 40{,}000)}{427} = 56.83 \text{ Cal/kg}$$

and, therefore,

$$Q = Gq = 6{,}470.6 \times 56.83 = 368{,}000 \text{ Cal},$$

and the time needed to raise the pressure to 16 ata

$$\tau = \frac{368{,}000}{4{,}200} = 87.5 \text{ min.}$$

In view of the insignificant value of x it would have been possible, in practice, to assume that $x_1 = x_2 = 0$, which would have made the calculation much simpler but a little less accurate. If this assumption is made, then

$$q = i_2' - i_1' - Av_x\,(p_2 - p_1) =$$

$$= 204 - 143.7 - \frac{0.001855\,(160{,}000 - 40{,}000)}{427} = 55 \text{ Cal/kg},$$

$$Q = 6{,}470.6 \times 55 = 356{,}000 \text{ Cal},$$

and the time needed

$$\tau = \frac{356{,}000}{4{,}200} = 84.6 \text{ min.}$$

The graphical method of solution cannot be used in this example because the process cannot be plotted in an *is* diagram (the area of the wet mixture is not included).

Example 12-2. 1 cum of dry saturated steam at a pressure of 10 ata is cooled at constant volume to 60° C. Determine the final quality of the steam, its final pressure and the amount of heat given up by it.

The constant specific volume $v_x = v_1'' = 0.198$ cum-kg; by equation 11-3

$$v_x = v_2' + x_2\,(v_2'' - v_2'),$$

whence,

$$x_2 = \frac{v_x - v_2'}{v_2'' - v_2'} = \frac{0.198 - 0.001}{7.678 - 0.001} = 0.0256,$$

i. e., at the end of the cooling process the mixture consists of 2.56% steam and 97.44% water by weight.

The pressure of the mixture at $t_2 = 60°$ C by the data in the tables is $p_2 = 0.2031$ ata.

From the tables of saturated steam we find

$$i_1'' = 663.3 \text{ Cal/kg};$$

$$i_{2_x} = i_2' + x_2 r_2 = 59.98 + 0.0256 \times 563.2 = 74.38 \text{ Cal/kg};$$

by equation 12-1

$$q = 74.38 - 663.3 - \frac{0.198\,(2{,}031 - 100{,}000)}{427} = 543.46 \text{ Cal/kg},$$

The weight of the steam is

$$G = \gamma_1'' = 5.051 \text{ kg},$$

and the amount of heat given up by the steam during cooling

$$Q = Gq = 5.051 \times 543.46 = -2{,}740 \text{ Cal}.$$

(The minus sign shows that the heat is given up by the steam).

For the same reason as that given in the first example the *is* diagram cannot be used for the solution of this example.

Example 12-3. Superheated steam at a pressure of 2 ata and a temperature of 160° C is heated at constant volume to a pressure of 3 ata. Determine the final temperature of the steam and the amount of heat required to superheat it.

From the *is* diagram we get the initial state represented by the point of intersection of the isobar $p_1 = 2$ ata and the isotherm $t_1 = 160°$ C:

$$v = 1 \text{ cum-kg and } i_1 = 666 \text{ Cal/kg},$$

and for the point of intersection of isochor $v = 1$ cum-kg and isobar $p_2 = 3$ ata

$$t_2 = 364° \text{ C and } i_2 = 764 \text{ Cal/kg}.$$

In this case by equation 12-1

$$q = 764 - 666 - \frac{1 \times (30{,}000 - 20{,}000)}{427} = 74.6 \text{ Cal/kg}.$$

The analytical calculation of this example is also quite simple if tables for superheated steam are used. For $p_1 = 2$ ata and $t_1 = 160°$ C we find directly from the tables that

$$v = 1.003 \text{ cum-kg and } i_1 = 666.4 \text{ Cal/kg}$$

and for $p_2 = 3$ ata and $v = 1.003$ cum-kg

$$t_2 \approx 370° \text{ C and } i_2 \approx 763.7 \text{ Cal/kg}.$$

The last figure is more accurate than that obtained from the diagram.

Example 12-4. Dry saturated steam at a pressure of 10 ata is heated in a closed vessel to 300° C. Determine the superheat of the steam at the end of the process.

From the *is* diagram we find that the initial state, represented by the point of intersection of the isobar $p_1 = 10$ ata and the threshold curve $x = 1$, is

$$v = v_1'' = 0.2 \text{ cum-kg}$$

and that the point of intersection of the isochor $v = 0.2$ cum-kg and isotherm $t_2 = 300°$ C is

$$p_2 = 13 \text{ ata}$$

The isotherm $t_{s2} = 190°$ C passes through the point of intersection of the isobar $p_2 = 13$ ata and the threshold curve $x = 1$; the superheat of the steam at $t_2 = 300°$ C, is, therefore,

$$t_2 - t_{s2} = 300 - 190 = 110° \text{ C}.$$

This solution may also be found simply by using the tables for superheated steam. From the tables we find that for $p_1 = 10$ ata and $x = 1$

$$v = v_1'' = 0.198 \text{ cum-kg}$$

and for $v = 0.198$ cum-kg and $t_2 = 300°$ C,

$$p_2 = 13 \text{ ata and } t_{s2} = 190.7° \text{ C}.$$

12-2. The Isobaric Process. Figs. 12-4, 12-5 and 12-6 are the *pv*, *Ts* and *is* diagrams for an isobaric process for the more common case of the type "c".

In the *pv* system the process is represented by a section of a horizontal line; it is also horizontal in the area of saturation in the *Ts* diagram, because when the pressure of saturated steam is constant the temperature is also constant, i. e., the isobaric process is also isothermic, but in the superheat area the isobar is a concave curve rising from left to right like that of a gas isobar. In the *is* system the isobar is an inclined straight iine in the area of saturation and in the area of superheat it is a concave curve and rising somewhat more steeply than the straight-line isobar in the area of wet steam.

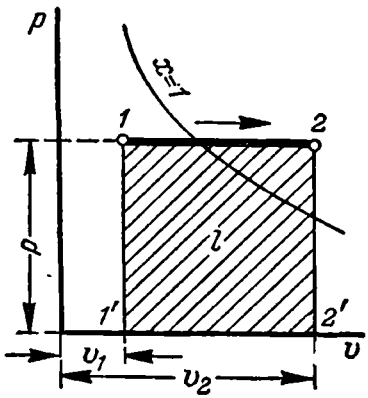


Fig. 12-4

The amount of heat imparted to the steam during the process is

$$q = i_2 - i_1; \qquad (12\text{-}2)$$

in the *Ts* system it is represented by the area below the isobar, 122′1′, and in the *is* system as the difference in the ordinates of points 2 and 1.

The work is

$$l = p(v_2 - v_1) \qquad (12\text{-}3)$$

and in the *pv* system it is represented by the area below the isobar, i. e., the area of the rectangle 122′1′.

The change in the internal energy during the process may be determined as

$$u_2 - u_1 = q - Al = i_2 - i_1 - Ap(v_2 - v_1). \qquad (12\text{-}4)$$

Calculations employing the *is* diagram give directly the values of i_1, i_2, v_1, v_2 and p, which are employed in equations 12-2, 12-3 and 12-4.

For an analytical calculation the value of the enthalpy for saturated steam is found by using equation 11-25:

$$i_x = i' + xr,$$

where $x \approx \frac{v_x}{v''}$, and the values of i', r and v'' are taken from the tables for saturated steam. The enthalpy of superheated steam

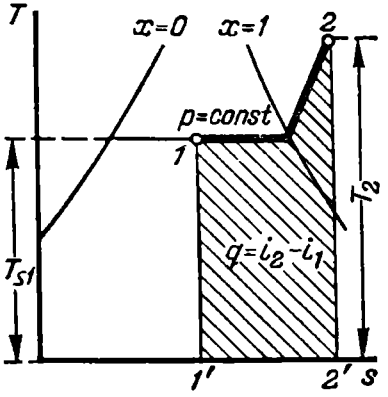


Fig. 12-5

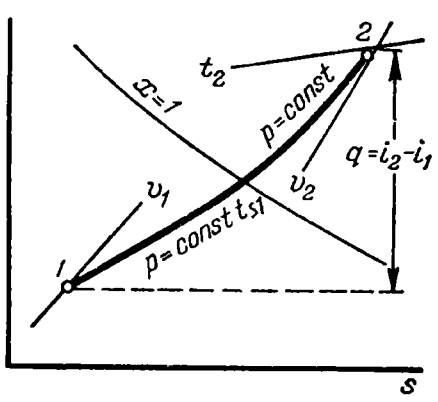


Fig. 12-6

is taken from the relevant tables using any pair of the parameters p, v and t.

If an isobaric process takes place entirely in the area of saturation, since p=const, i'=const and r=const,

$$q = i_{x_2} - i_{x_1} = i' + x_2 r - (i' + x_1 r) = r(x_2 - x_1). \quad (12\text{-}5)$$

Example 12-5. What quantity of heat must be imparted to each kilogram of steam with 10% humidity at a pressure of 8 ata to bring it up to dry saturation at constant pressure?

From the *is* diagram we find that i_1=612 Cal/kg and i_2=661 Cal/kg.

By equation 12-2, $q = i_2 - i_1 = 661 - 612 = 49$ Cal/kg or, analytically, by equation 12-5

$$q = r(x_2 - x_1) = 489.8(1 - 0.9) = 48.98 \text{ Cal/kg}.$$

Example 12-6. Superheated steam at 200° C is heated at a constant pressure of 6 ata to 300° C. Determine the expenditure of heat in the process, the work of expansion and the change in the internal energy of the steam.

From the *is* diagram we find

i_1 = 681 Cal/kg; i_2 = 731 Cal/kg;

v_1 = 0.36 cum-kg; v_2 = 0.45 cum-kg;

by equation 12-2

$$q = 731 - 681 = 50 \text{ Cal/kg};$$

by equation 12-3

$$l = 60{,}000\,(0.45 - 0.36) = 5{,}400 \text{ kgm/kg}$$

and the change in the internal energy by equation 12-3 is

$$u_2 - u_1 = q - Al = 50 - \frac{5{,}400}{427} = 50 - 12.6 = 37.4 \text{ Cal/kg}.$$

With the aid of tables for superheated steam we get a more accurate solution:

$$i_1 = 680.6 \text{ Cal/kg}; \quad i_2 = 730.7 \text{ Cal/kg}; \quad v_1 = 0.3591 \text{ cum-kg};$$

$$v_2 = 0.4428 \text{ cum-kg}; \quad q = 730.7 - 680.6 = 50.1 \text{ Cal/kg};$$

$$l = 60{,}000\,(0.4428 - 0.3591) = 5{,}022 \text{ kgm/kg};$$

$$u_2 - u_1 = 50.1 - \frac{5{,}022}{427} = 38.35 \text{ Cal/kg}.$$

12-3. The Isothermic Process. Figs. 12-7, 12-8 and 12-9 are the *pv*, *Ts* and *is* diagrams for an isothermic case (of the more general case, type "c").

In the *pv* system the process is represented in the area of saturation by a section of a horizontal line because the p and t_s of saturated steam are constant, i. e., the isothermic process is also isobaric, and in the area of superheat it is a hyperbolic curve closer to the horizontal than an equilateral hyperbola (the gas isotherm). In the *Ts* system the process is represented by a section of a horizontal line and in the *is* system by an inclined straight line in the area of saturation (which is also an isobar) and, in the area of superheat, by a convex curve rising slightly from left to right and, as it leaves the upper threshold curve, asymptotically approaching the horizontal.

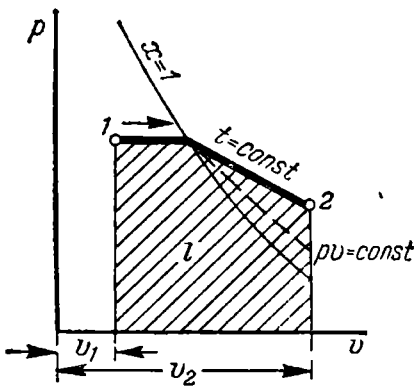


Fig. 12-7

The amount of heat imparted to the steam during the process is

$$q = T\,(s_2 - s_1); \qquad (12\text{-}6)$$

it is represented in the *Ts* diagram by the area 122′1′.

The change in the internal energy (the work of dissipation) is

$$u_2 - u_1 = i_2 - Ap_2v_2 - (i_1 - Ap_1v_1) = \\ = i_2 - i_1 - A(p_2v_2 - p_1v_1). \qquad (12\text{-}7)$$

The work of expansion

$$Al = q - (u_2 - u_1) = \\ = T(s_2 - s_1) - (i_2 - i_1) + A(p_2v_2 - p_1v_1). \qquad (12\text{-}8)$$

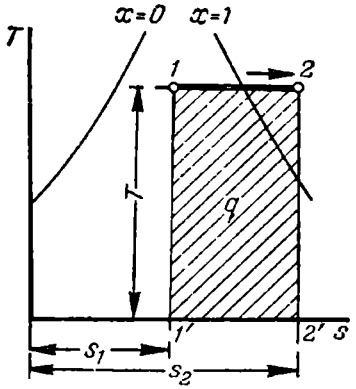


Fig. 12-8

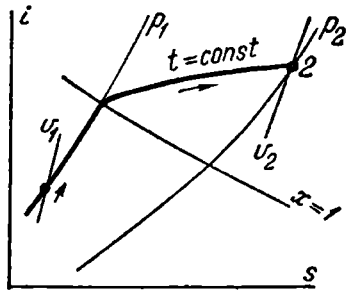


Fig. 12-9

Example 12-7. Steam at a temperature of 200° C expands isothermically from a pressure of 5 to 1 ata. Determine the amount of heat imparted to the steam, the change in internal energy and the work of expansion.

From the *is* diagram we find that

$i_1 = 682$ Cal/kg; $i_2 = 687$ Cal/kg; $v_1 = 0.43$ cum-kg; $v_2 = 2.25$ cum-kg; $s_1 = 1.688$ Cal/kg × deg; $s_2 = 1.87$ Cal/kg × deg.

Then, by equation 12-6

$$q = 473(1.87 - 1.688) = 86 \text{ Cal/kg};$$

and by equation 12-7

$$u_2 - u_1 = 687 - 682 - \frac{10{,}000 \times 2.25 - 50{,}000 \times 0.43}{427} = 2.66 \text{ Cal/kg}$$

and by equation 12-8

$$Al = 86 - 2.66 = 83.34 \text{ Cal/kg}.$$

More precisely, using the superheated steam tables:

$i_1 = 681.7$ Cal/kg; $i_2 = 686.6$ Cal/kg; $v_1 = 0.4334$ cum-kg; $v_2 = 2.214$ cum-kg; $s_1 = 1.6875$ Cal/kg/deg; $s_2 = 1.8717$ Cal/kg/deg;

$$q = 473\,(1.8717 - 1.6875) = 87 \text{ Cal/kg};$$

$$u_2 - u_1 = 686.6 - 681.7 - \frac{10{,}000 \times 2.214 - 50{,}000 \times 0.4334}{427} = 3.8 \text{ Cal/kg};$$

$$Al = 87 - 3.8 = 83.2 \text{ Cal/kg}.$$

Thus, we see that there is some dissipation in cases of superheated steam even if it is insignificant; the internal energy of superheated steam, therefore, is a function not only of the temperature but also of the volume (or pressure).

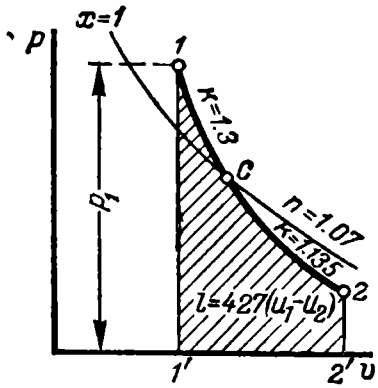


Fig. 12-10

12-4. The Adiabatic Process. Figs. 12-10, 12-11 and 12-12 represent a reversible adiabatic process (for the more general case "c") in *pv*, *Ts* and *is* diagrams.

In the *Ts* and *is* systems the process is represented by a section of a vertical line because s=const in a reversible adiabatic process; in the *pv* system it is a hyperbolic curve which, allowing for some approximation, may be expressed by the equation $pv^k = \text{const}$, where k is a purely empiric exponent with different values for superheated and saturated

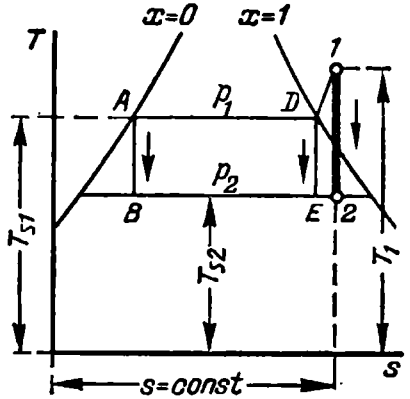


Fig. 12-11

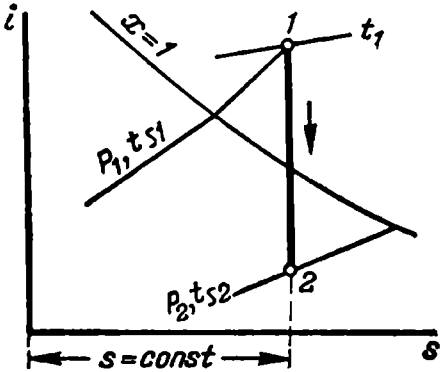


Fig. 12-12

vapour; for steam the approximate mean value of k for the area of superheat (adiabatic 1-C) is $k = 1.3$ and for the area

of saturation (adiabatic C-2) it is $k=1.135$, i. e., the curve 1-C is somewhat closer to the vertical than curve C-2 so that the adiabatic curve 1-2 as a whole is broken at point C where it intersects the upper threshold curve. It must be remembered that these values of the exponent are averages and are only approximations so that they must not be used for precise calculations.

It can be seen from the diagrams that adiabatic expansion of superheated steam is a case of a reduction in the superheat during which the steam becomes wet steam, i. e., it is partially condensed; this phenomenon is closely connected with the negative heat capacity of the dry steam c'' of the majority of substances. From Fig. 12-11 we see that in the case of the adiabatic expansion of the liquid (adiabatic AB), part of it is converted into steam. If the quality of the steam for a number of adiabatic curves between AB and DE is determined from the Ts diagram within the temperature limits T_{s1} and T_{s2}, then we see that for steam at $x_1<0.5$ the expansion accompanies the formation of steam, i. e., $x_2>x_1$, and when $x_1>0.5$ the expansion is accompanied by condensation, i. e., $x_2<x_1$. A mixture of low quality (point B) can be reduced to a liquid by adiabatic compression and high-quality steam (point 2) into dry saturated and superheated steam.

For the adiabatic process

$$Al=u_1-u_2=i_1-Ap_1v_1-(i_2-Ap_2v_2)=$$
$$=i_1-i_2-A(p_1v_1-p_2v_2). \qquad (12\text{-}9)$$

If it be assumed that the adiabatic is expressed by the equation $pv^k=\text{const}$, the work could be determined from equations 4-26, 4-28 and 4-29 as for gases:

$$l=\frac{1}{k-1}(p_1v_1-p_2v_2)=\frac{p_1v_1}{k-1}\left[1-\left(\frac{v_1}{v_2}\right)^{k-1}\right]=$$
$$=\frac{p_1v_1}{k-1}\left[1-\left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}\right]. \qquad (12\text{-}10)$$

In the case represented by Fig. 12-10 the work would have to be calculated separately for sections 1-C and C-2 because the value of k for each of them is different; the value of the pressure and volume at point C on the upper threshold curve must be found. This method of calculation is obviously

more complicated than the application of equation 12-9 and, furthermore, is less accurate.

Example 12-8. Dry saturated steam expands adiabatically from 7 to 1 ata. Determine the work of expansion.

From the *is* diagram we find that

$i_1'' = 660$ Cal/kg; $v_1'' = 0.28$ cum-kg; $i_{x2} = 581$ Cal/kg; $v_{x2} = 1.6$ cum-kg

so that by equation 12-9

$$Al = 660 - 581 - \frac{70{,}000 \times 0.28 - 10{,}000 \times 1.6}{427} = 70.57 \text{ Cal/kg}$$

and

$$l = 427 \times 70.57 = 30{,}200 \text{ kgm/kg},$$

and by equation 12-10

$$l = \frac{p_1 v_1''}{k-1}\left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}\right] = \frac{70{,}000 \times 0.2778}{1.135-1}\left[1 - \left(\frac{1}{7}\right)^{\frac{0.135}{1\ 135}}\right] =$$

$$= 29{,}600 \text{ kgm/kg}.$$

Example 12-9. A mixture of steam and water whose quality is 7.2% at a pressure of 2 ata is compressed adiabatically until it becomes all water. Determine the work of compression.

The *is* diagram cannot be used; the calculation must be made analytically. From the relation $s_{x1} = s_2'$, we find from the saturated steam tables that

$$s_2' = s_1' + \frac{x_1 r_1}{T_{s_1}} = 0.363 + 0.072\,(1.7039 - 0.3639) = 0.46 \text{ Cal/kg} \times \text{deg};$$

from the tables we find with sufficient accuracy ($s_2' = 0.4594$ Cal/kg$\times$deg) that

$$p_2 = 6 \text{ ata}.$$

Continuing to apply the tables

$$i_1' = 119.94 \text{ Cal/kg}; \quad r_1 = 526.4 \text{ Cal/kg}; \quad i_2' = 159.3 \text{ Cal/kg};$$
$$v_1' = 0.00106 \text{ cum-kg}; \quad v_1'' = 0.9018 \text{ cum-kg}; \quad v_2' = 0.0011 \text{ cum-kg};$$

so that

$$i_{x1} = i_1' + x_1 r_1 = 119.94 + 0.072 \times 526.4 = 157.84 \text{ Cal/kg};$$
$$v_{x1} = v_1' + x_1\,(v_1'' - v_1') = 0.00106 + 0.072\,(0.9018 - 0.00106) =$$
$$= 0.066 \text{ cum-kg},$$

and, by equation 12-9

$$Al = 157.84 - 159.3 - \frac{20{,}000 \times 0.066 - 60{,}000 \times 0.0011}{427} = -4.4 \text{ Cal/kg};$$

the minus sign shows that the work is expended externally (the work of compression).

Example 12-10. Superheated steam at an initial pressure of 7 ata and a temperature of 220° C expands adiabatically to a pressure of 0.2 ata. Determine the work of expansion.

From the *is* diagram we find

$i_1 = 690$ Cal/kg; $v_1 = 0.3225$ cum-kg; $i_{x2} = 550$ Cal/kg; $v_{x2} = 6.5$ cum-kg.

By equation 12-9, therefore,

$$Al = 690 - 550 - \frac{70{,}000 \times 0.3225 - 2{,}000 \times 6.5}{427} = 117.6 \text{ Cal/kg}.$$

Example 12-11. Superheated steam at 10 ata, during adiabatic expansion to a pressure of 2.5 ata is converted into dry saturated steam. Determine the initial superheat of the steam.

Through the point of intersection of the isobar $p_2 = 2.5$ ata and the upper threshold curve ($x_2 = 1$) in the *is* diagram, we plot a vertical straight line to the point of intersection with isobar $p_1 = 10$ ata; the isotherm $t_1 = 280°$ C passes through this point. From the saturated steam tables we find that $t_{s1} = 179°$ C so that the initial superheat of the steam $t_1 - t_{s1} = 280 - 179 = 101°$ C.

12-5. The Streaming and Throttling of a Vapour. The basic theses of the theory of streaming which we deduced in chapter nine are also valid for dry vapours. In particular, the available work in the general case (equation 9-9) is

$$Al_0 = q + i_1 - i_2;$$

it may be represented as an area in a *Ts* diagram.

For a reversible superheated steam process *AB* (Fig. 12-13) we get:

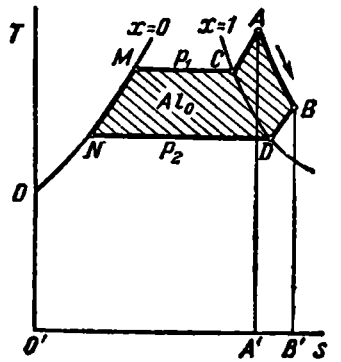


Fig. 12-13

$i_1 = \text{area } OMCAA'O'$; $i_2 = \text{area } ONDBB'O'$; $q = \text{area } ABB'A'$

so that

$$Al_0 = q + i_1 - i_2 = \text{area } OMCABB'O' - \text{area } ONDBB'O' = \text{area } MCABDN,$$

i. e., the available work of the steam is represented in the Ts diagram as the area between the curve of the process, the lower threshold curve and the extreme isobars. Thus, we see that we have here complete accordance with the *pv* system

in which the available work is represented as the area between the curve of the process, the axis of the ordinate and the extreme isobars, while the lower threshold curve practically coincides with the axis of the ordinate.

What has been said in this paragraph is true only of reversible streaming processes, since it is only for them that the area below the curve of the process in the *Ts* system gives the amount of heat q.

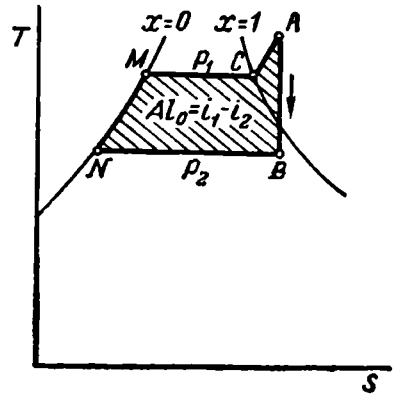


Fig. 12-14

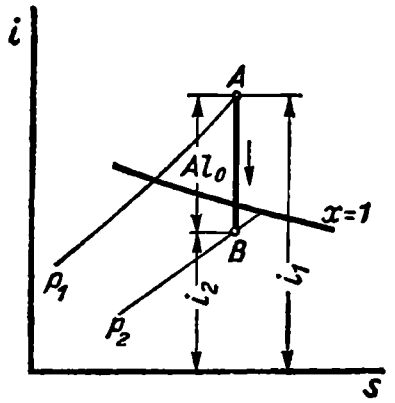


Fig. 12-15

Figs. 12-14 and 12-15 represent a reversible adiabatic process AB in the *Ts* and *is* diagrams.

The available work

$$Al_0 = i_1 - i_2$$

is equal to the area $MCABN$ in the *Ts* diagram and the length of the adiabatic AB in the *is* diagram. In this instance the advantage of the *is* diagram is obvious—the area of the figure below the curve does not have to be measured.

The critical relation of the pressure, by equation 9-19, is

$$\frac{p_{cr}}{p_1} = \left(\frac{2}{k+1}\right)^{\frac{k}{k-1}},$$

where k is the exponent of the adiabatic. Giving k the approximated values of 1.3 for superheated steam and 1.135 for dry saturated steam (at the beginning of the expansion) we get:

for the superheated steam

$$\frac{p_{cr}}{p_1} = 0.546; \qquad (12\text{-}11)$$

for dry saturated steam (at the beginning of the expansion)

$$\frac{p_{cr}}{p_1} = 0.577. \tag{12-12}$$

The critical velocity of the stream by equation 9-21 is

$$c_{cr} = \sqrt{2g \frac{k}{k+1} p_1 v_1};$$

and, on the above assumption ($k = 1.3$), for superheated steam

$$c_{cr} = 3.33 \sqrt{p_1 v_1}; \tag{12-13}$$

and for dry saturated steam (at the beginning of the expansion)

$$c_{cr} = 3.23 \sqrt{p_1 v_1''}, \tag{12-14}$$

where the pressure, p_1, is expressed in kg-sqm. Since the threshold curve for dry saturated steam is slightly nearer the vertical than an equilateral hyperbola, the product $p_1 v_1''$ and the velocity c_{cr} are little changed by changes in pressure.

The critical velocity of superheated steam is greater than that of saturated steam at the same pressure because the coefficient preceding the root is bigger and $v_1 > v_1''$; depending on the pressure and temperature the value of c_{cr} changes within the limits of 450 to 650 metres per second.

Cross-section f_{min}, which corresponds to velocity c_{cr} is, by equation 9-22,

$$f_{min} = \frac{G}{\left(\frac{2}{k+1}\right)^{\frac{1}{k-1}} \sqrt{2g \frac{k}{k+1} \times \frac{p_1}{v_1}}};$$

allowing the former assumption:

for superheated steam ($k = 1.3$)

$$f_{min} = \frac{G}{2.09 \sqrt{\frac{p_1}{v_1}}} \text{ sqm}; \tag{12-15}$$

for dry saturated steam (at the beginning of the expansion)

$$f_{min} = \frac{G}{1.99 \sqrt{\frac{p_1}{v_1''}}} \text{ sqm}. \tag{12-16}$$

A real streaming process is always accompanied by friction and, consequently, by a loss of work. Since friction makes the adiabatic process irreversible there is an increase in entropy and it is depicted in the *Ts* and *is* diagrams by the curve *AB* which is somewhat approximated (Figs. 12-16 and 12-17). According to equation 9-10 which is true for both

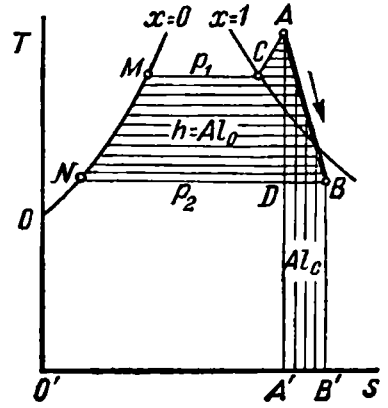


Fig. 12-16

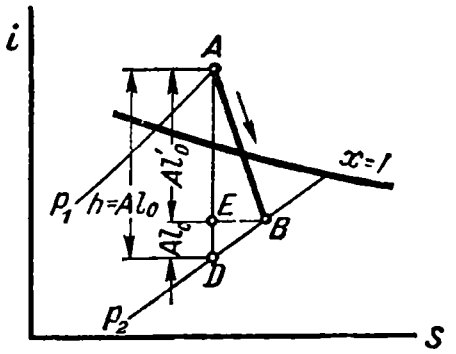


Fig. 12-17

reversible and irreversible processes, the available work from adiabatic reversible expansion *AD* (without friction) is

$$Al_0 = A\frac{c^2}{2g} = i_a - i_d = h$$

and is represented in the *Ts* system by the area *MCADN* and in the *is* system by the length of the adiabatic *AD*. The available work in a real process of expansion *AB* (with friction) by the same equation 9-10 will be

$$Al_0' = A\frac{c'^2}{2g} = i_a - i_b.$$

Since $i_b > i_d$, then $Al_0' < Al_0$ and $c' < c$. The losses from friction in the available work are

$$Al_c = Al_0 - Al_0' = i_a - i_d - (i_a - i_b) = i_b - i_d,$$

and are represented in the *Ts* system by the area *DBB'A'* and in the *is* system as a section of the vertical line $\overline{ED}$. As far as the real available work, Al_0', is concerned, it is represented in the *Ts* system as the difference in the areas *MCADN* and *DBB'A'*, Al_0' being equal $Al_0 - Al_c$; in the *is*

system it is the difference in the sections of the line $\overline{AD}$ and $\overline{ED}$, i. e., the vertical section $\overline{AE}$. Here, again, we see the value of the *is* diagram.

The velocity of the stream corresponding to the drop in heat $Al_0'=i_a-i_b$ by equation 9-12 is

$$c'=91.5\sqrt{i_a-i_b};$$

it is less than the theoretical $c=91.5\sqrt{h}$ so that we may write

$$c'=\varphi c,$$

where φ is the *velocity coefficient of the nozzle*, it is less than unity and equal to an average of 0.95 for steam turbines.

The loss of work through friction causes a reduction in the final velocity of the stream and may be expressed as follows:

$$l_c=\frac{c^2}{2g}-\frac{c'^2}{2g}=\frac{c^2}{2g}\left[1-\left(\frac{c'}{c}\right)^2\right]=\frac{c^2}{2g}(1-\varphi^2)=\zeta\frac{c^2}{2g},$$

which in heat units is

$$Al_c=A\zeta\frac{c^2}{2g}=\zeta Al_0=\zeta h, \qquad (12\text{-}17)$$

where $\zeta=1-\varphi^2$ and is known as the *coefficient of energy loss in the nozzle.*

If, therefore, we are given the initial and final state of the steam, i. e., the points A and B in the *is* diagram (Fig. 12-17), by plotting a horizontal line through point B to the point of its intersection at point E with a vertical drawn through point A, we get the loss Al_c in the form of a section of the vertical line $\overline{ED}$, and the coefficient of energy loss as the relation $\zeta=\frac{Al_c}{Al_0}=\frac{\overline{ED}}{\overline{AD}}$. If the initial point A and the coefficient ζ are given, by plotting the section $\overline{DE}$ ζh from point D and drawing a horizontal line through point E we get the final point of the process B at its intersection with the isobar p_2 which gives us the specific volume v_2 necessary to find the cross-section of the nozzle outlet f_2. As we shall see, it is not necessary to know the real nature of the curve AB, i. e., its intermediate points, for the calculation of the nozzle.

If the stream passes through a narrow place in the nozzle and is throttled, the change in its state is best shown in an

is diagram (Fig. 12-18) because the initial and final points lie on the same horizontal line on account of the basic condition of the process being $i_1=i_2$. From the diagram it can be seen that wet steam (point A_1) becomes drier when throttled and dry saturated steam (point A_2) becomes superheated while superheated steam (point A_3) increases its superheat.

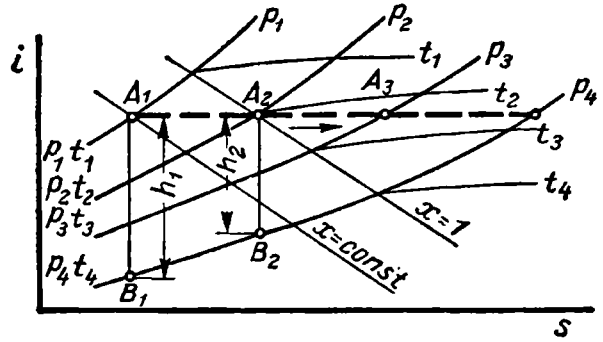


Fig. 12-18

From the nature of the upper threshold curve in the *is* system and the position of the critical point *k* (Fig. 12-19) it can, however, be seen that when throttled, superheated steam at high pressure and relatively low superheat, for example in the state indicated by point A_1, at first turns into dry saturated (point A_2) and then into wet steam, and as the throttling increases it gets drier (point A_3) and again becomes superheated steam at point A_4. From Fig. 12-19 it can also be seen that when liquid at boiling point is throttled (point *B*) it becomes steam.

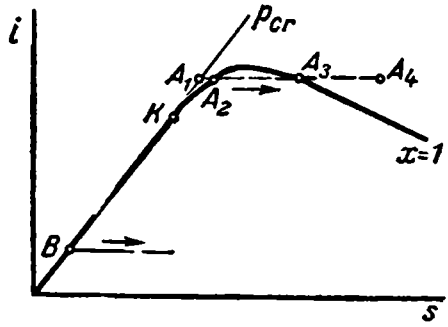


Fig. 12-19

When steam is throttled its temperature drops; in the area of saturation this is quite obvious since the lower pressure of saturated steam corresponds to a definitely lower temperature; thus, for example, when steam in the state indicated by point A_1 (Fig. 12-18) is throttled down to pressure p_2 (point A_2) the temperature drops from t_1 to t_2. In the area

of superheated steam the drop in temperature due to throttling is not so strongly felt; thus, for example, when superheated steam is throttled from pressure p_2 (point A_2) to pressure p_3 (point A_3) the temperature falls to some intermediate value between t_2 and t_3; in the case of saturated steam the temperature would have fallen to t_3. The drop in the temperature of superheated steam is the less the greater the superheat, because the isotherm of superheated steam straightens out the farther it extends from the upper threshold curve until it becomes almost horizontal.

Depending on pressure and temperature, the drop in temperature of superheated steam is

$$\Delta t = 0.7\Delta p\text{-}3\Delta p\ [°C]$$

where Δp is expressed in kg-sqcm.

We may assume the same for superheated vapours as we did for gases, i. e., that

$$p_2 v_2 = p_1 v_1$$

will be a sufficiently accurate approximation; for superheated steam, for instance, $i_2 = i_1 = 700$ Cal/kg and

$p =$	50	20	8	6 ata
$pv =$	2.32	2.34	2.34	2.36 kgm/kg.

Like every irreversible process throttling involves a loss of available work as can be seen from Fig. 12-18. The steam at point A_1, the initial state, suffers a loss of heat, h_1, during its adiabatic expansion to presure p_4. After throttling to pressure p_2 (point A_2), despite the fact that the original heat content is retained, the drop in heat during expansion to the same pressure p_4 is reduced to h_2; the greater the throttling the greater the loss of available work.

Example 12-12. Superheated steam at pressure $p_1 = 14$ ata and temperature $= 400°$ C is expanded adiabatically to $p_2 = 2.5$ ata. Calculate the nozzle.

$$p_{cr} = 0.546 p_1 = 0.546 \times 14 = 7.65 \text{ ata} > p_2,$$

i. e., the nozzle must widen towards the outlet.

From the *is* diagram the loss of heat $h = 104$ Cal/kg so that the velocity of the ejection of the steam from the nozzle, by equation 9-12, is

$$c_2 = 91.5 \sqrt{104} = 943 \text{ m/sec.}$$

From the same diagram the specific volume in the outlet section is

$$v_2 = 0.8 \text{ cum-kg.}$$

The cross-section of the outlet is

$$f_2 = \frac{Gv_2}{c_2} = \frac{0.8}{943} G = 0.00085\,G \text{ sqm}$$

and the narrowest cross-section by equation 12-15 will be

$$f_{\min} = \frac{G}{2.09\sqrt{\frac{p_1}{v_1}}} = \frac{G}{2.09\sqrt{\frac{140{,}000}{0.222}}} = 0.0006\,G \text{ sqm},$$

and, therefore,

$$\frac{f_2}{f_{\min}} = \frac{0.00085G}{0.0006G} = 1.4.$$

Example 12-13. Dry saturated steam at a pressure of 12 ata is expanded in a nozzle to 4 ata and ejected at 6% humidity. Determine the true velocity of ejection and the losses in the nozzle.

From the *is* diagram we find the values of the points in Fig. 12-17

$$i_a = 665 \text{ Cal/kg}; \quad i_b = 623 \text{ Cal/kg}; \quad i_d = 617 \text{ Cal/kg};$$

therefore

$$c' = 91.5\sqrt{i_a - i_b} = 91.5\sqrt{665 - 623} = 593 \text{ m/sec}.$$

The loss of heat

$$Al_c = i_b - i_d = 623 - 617 = 6 \text{ Cal/kg}$$

and since the theoretical heat collapse is

$$h = i_a - i_d = 665 - 617 = 48 \text{ Cal/kg},$$

the coefficient of energy loss in the nozzle will be (equation 12-17)

$$\zeta = \frac{Al_c}{h} = \frac{6}{48} = 0.125,$$

i. e., 12.5% of the heat loss is due to friction.

Example 12-14. Steam with an original state of $p = 10$ ata and $t = 350°$ C is expanded in a nozzle to a pressure of 6 ata. Calculate the nozzle if the coefficient of velocity is $\varphi = 0.95$.

Since the steam in its original state is superheated

$$p_{cr} = 0.546 \times 10 = 5.46 \text{ ata} < p_2,$$

i. e., the nozzle must narrow towards the outlet so that it will be sufficient to determine f_2.

The theoretical loss of heat from the *is* diagram is

$$h = 32 \text{ Cal/kg},$$

the coefficient of energy loss of the stream is

$$\zeta = 1 - \varphi^2 = 1 - 0.95^2 = 0.1$$

so that the loss in the nozzle is

$$Al_c = \zeta h = 0.1 \times 32 = 3.2 \text{ Cal/kg}.$$

Plotting this in the diagram as the section of the vertical straight line $\overline{DE}$ (Fig. 12-17) and constructing a horizontal line through point E, at its intersection with isobar $p_2 = 6$ ata we find point B whose volume is $v_2 = 0.4$ cum-kg.

The true loss of heat is

$$Al_0' = h - Al_c = 32 - 3.2 = 28.8 \text{ Cal/kg},$$

and the velocity corresponding to it is

$$c_2 = 91.5 \sqrt{28.8} = 492 \text{ m/sec},$$

and the cross-sectional area of the outlet is

$$f_2 = \frac{Gv_2}{c_2} = \frac{0.4}{492} G = 0{,}000812G \text{ sqm}.$$

Example 12-15. Superheated steam at a pressure of 35 ata and a temperature of 350° C is throttled when passing through a narrow valve to a pressure of 25 ata. Determine the temperature of the steam after passing the valve and the loss of heat when it is expanded to 0.1 ata.

Plotting a horizontal line through the point of intersection of the isobar $p_1 = 35$ ata and the isotherm $t_1 = 350°$ C in the *is* diagram and extending it to its point of intersection with isobar $p_1' = 25$ ata, we find that temperature $t_1' = 340°$ C. From this diagram we find that

$$h_1 = 238 \text{ Cal/kg and } h_1' = 226 \text{ Cal/kg};$$

the relative loss is

$$\frac{h_1 - h_1'}{h_1} = \frac{238 - 226}{238} = 0.0505,$$

i. e., more than 5%.

Chapter Thirteen

THE CYCLES OF STEAM ENGINES

13-1. The Carnot Cycle for Saturated Vapour. In chapter five we established the fact that the most economical method of converting heat into work within certain temperature limits was the Carnot cycle, the efficiency of which does not depend on the nature of the working substance. It is, therefore, only natural that we should try to put the Carnot cycle into operation in a steam engine, at least theoretically, and work with the saturated vapour of water, or steam, since this is the simplest and most easily obtainable working substance.

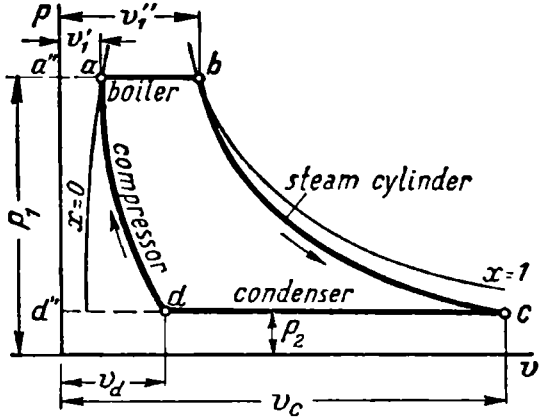


Fig. 13-1

Such a cycle, realised in its entirety in the area of saturation, is depicted in *pv* and *Ts* diagrams in Figs. 13-1 and 13-2. The isothermic process AB is a process of steam formation at constant pressure p_1 and the corresponding temperature T_{s1}, with boiling water at point A and dry saturated steam at point B; the latter is then expanded adiabatically, BC, during which process it becomes humid. During the

isothermic process CD, heat is taken from the wet steam at constant pressure p_2 which corresponds to temperature T_{s2}, and the greater part of the steam is condensed and becomes water. The cycle is completed by the adiabatic compression DA, as a result of which the mixture of steam and water in the state indicated by point D is converted in its entirety into water in the state indicated by point A, i.e., at temperature T_{s1}, and pressure p_1.

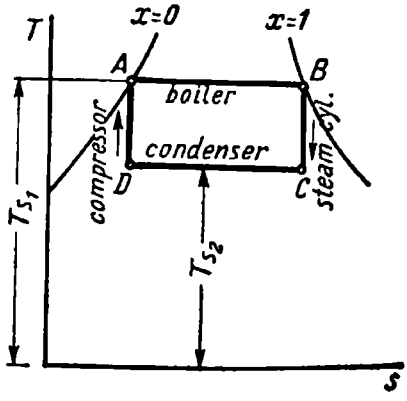


Fig. 13-2

In practice it is obviously impossible to effect the four processes of the Carnot cycle in a single working space, for example in the cylinder of a steam engine or in a steam turbine—so that the process must be divided into a number of parts. The installation represented schematically in Fig. 13-3, however, is feasible; it works as follows.

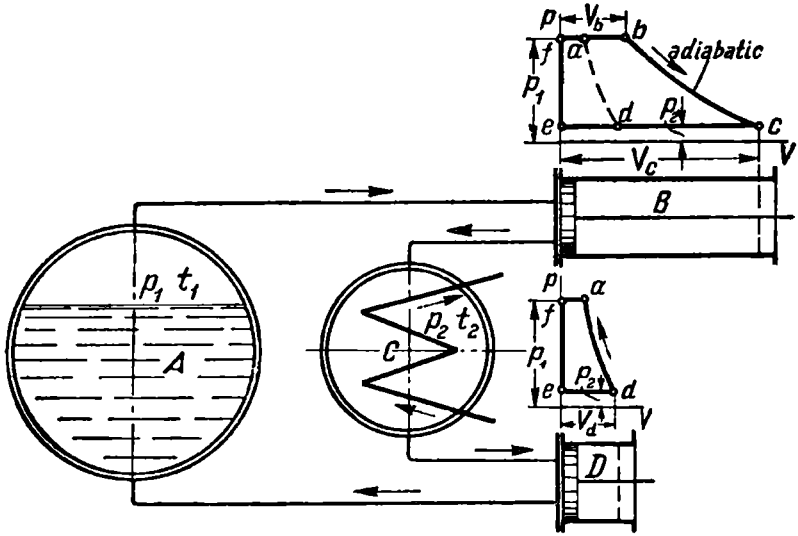


Fig. 13-3

The process of steam formation AB takes place in the steam boiler A, from which dry saturated steam at pressure p_1 enters the cylinder B of the engine by way of a steam pipe

which injects it into the left-hand part of cylinder as shown in Fig 13-3, the quantity of steam being G kg. According to the process as we have established it, a similar amount of feed-water should be injected simultaneously into the boiler and be converted into dry saturated steam at pressure p_1, given this condition, the pressure of the steam in the boiler and in the cylinder at the time steam is injected into it will remain unchanged. If we plot a coordinate system pV whose abscissae are the volumes, V, in the cylinder and whose ordinates are the pressures, p, we obtain an *indicator diagram* similar to that in Sec. 7-3; in this diagram the period of steam injection into the cylinder is indicated by a section of a horizontal line fb, and its value, V_b, is obviously equal to Gv_1''. The volume of the steam, V_b, and consequently the amount by weight, G, that enters the cylinder must be computed in such a way that the steam, expanding from point b adiabatically, will reduce its pressure at the end of the piston stroke (point c = RDC) to pressure p_2 of the cycle; in this case the adiabatic expansion BC of the cycle is effected in the cylinder. On the return stroke of the piston the whole of the steam, $V_c = Gv_c$, is forced out of the cylinder into the condenser, C, through which a continuous stream of water is passed as a coolant. The condenser must be calculated in such a way that it produces a mixture of steam and water in the state indicated by point D (Fig. 13-2) when heat is taken from the steam. In accordance with the cycle, when G kg of waste steam enters the condenser, heat is taken from it and a similar weight of steam mixture with a high water content is removed from the condenser. Under these conditions the pressure in the condenser and, therefore, in the cylinder will remain unchanged during the exhaust stroke and will equal p_2. In accordance with this the period of the exhaust stroke is shown in the indicator diagram as the horizontal line ce. At point e, i. e., at LDC the inlet valve again opens allowing fresh steam to enter the cylinder from the boiler, instantaneously raising the pressure from p_2 to p_1 as shown by the vertical line ef; a further portion of steam weighing G kg enters the cylinder and the cycle is repeated.

The isothermic and, simultaneously, isobaric process CD is effected in the condenser; the mixture $V_d = Gv_d$ is sucked out of the condenser by a full stroke of the compressor piston D, beginning from LDC. Since the pressure in the con-

denser is unchangingly equal to p_2 the pressure in the cylinder during the suction stroke is p_2=const; in the indicator diagram of the compressor, therefore, the suction stroke is represented by the horizontal line *ed*. When the piston of the compressor reaches RDC the suction valve closes and on the return stroke of the piston the mixture is compressed adiabatically *da* to pressure p_1. At this pressure, as we see from Fig. 13-1, we get water in the compressor in the same state as that in the boiler; at point *a* the force valve opens, and by the end of the compressor piston stroke the water with a volume of $V_d=Gv_1$ is transmitted to the boiler at constant pressure p_1, where the heat of steam formation r_1 is imparted to it and it is converted into dry saturated steam, i. e., into steam in the same state and in the same quantity by weight, G kg, as that which entered the cylinder of the steam engine.

The period in which the compressor is driving the steam is shown in its indicator diagram as the horizontal line *af*; when the piston is at LDC (point *f*) the force valve closes and the suction valve reopens, connecting the compressor with the condenser, the pressure in the compressor instantaneously drops from p_1 to p_2 as represented by the vertical line *fe*, the piston moves to the right, drawing the mixture into the cylinder, and the compressor process is repeated. The adiabatic compression, *DA*, therefore takes place in the compressor.

As a result of the full cycle employing G kg of steam, work is done in the steam-engine cylinder which is equal to the area *fbce* in its indicator diagram, and work equal to area *fade* is expended on the compressor so that in the final analysis the positive work performed by the installation is equal to the difference in those two areas. By superimposing the indicator diagram of the compressor on that of the engine cylinder so that their axes coincide we get the work of the installation for one cycle (using G kg of steam) as the area *abcd* (Fig. 13-3).

In the case under discussion, the difference in the indicator work of the steam-engine cylinder and that of the compressor is equal to the work of the cycle of G kg of steam, as can easily be proved by comparing the closed figure *abcd* in Fig. 13-3 with the curve of the cycle for 1 kg of steam, *abcd* in Fig. 13-1. The only difference is in their abscissae, the former being G times greater than the latter so that the area of the former is also G times greater than that of the latter.

It is necessary to point out the essential difference between the indicator diagrams and the *pv* diagram of the cycle; the former show the differences in pressure that correspond to the position of the pistons in the respective cylinders while the latter shows changes in the state of the body, i. e., in the pressure and specific volume, in the course of the cycle in various parts of the installation. The latter refers to a definite quantity of the body by weight (usually 1 kg); each point in the indicator diagram, generally speaking, refers to a different weight of the working body in the cylinder. For example: during the suction stroke *fb* (Fig. 13-3) the amount of steam in the cylinder increases from zero at point *f* to *G* kg at point *b*, and during the exhaust stroke *ce* it decreases from *G* kg at point *c* to zero at point *e*. In the theoretical process the state of the steam does not change during the inlet and exhaust strokes so that the horizontal lines *fb* and *ce* (Fig. 13-3) do not indicate a change of state and, therefore, do not refer to the cycle. The adiabatic curve *bc*, which throughout its entire length refers to one and the same quantity of steam, *G* kg, is the only line representing a change in the state of the steam in the cylinder which corresponds to the adiabatic expansion *bc* of the cycle.

Similarly, in the indicator diagram only the line *da* indicates a change of state, i. e., adiabatic compression.

The thermal efficiency of the cycle is

$$\eta_t = 1 - \frac{T_{s2}}{T_{s1}},$$

and the work of the cycle is

$$Al = \eta_t q_1 = \left(1 - \frac{T_{s2}}{T_{s1}}\right) r_1$$

where r_1 — the heat of steam formation at pressure p_1.

As we have already seen, the application of the Carnot cycle requires the use of a compressor cylinder with a volume of V_d in addition to the steam cylinder with a volume of V_c; the relative sizes of the two cylinders may be judged from the following ratio:

$$\frac{V_d}{V_c} = \frac{Gv_d}{Gv_c} = \frac{v_d}{v_c}.$$

It can be seen from Fig. 13-1 that as the temperature T_{s1} rises, and with it the pressure p_1, this ratio becomes greater;

the ratio of the work of the compressor l_2 to that of the steam-engine cylinder, l_1, the ratio of area *a"add"* to area *a"bcd"* will also be greater. Since these two areas provide us with the value of the available work during processes *ad* and *bc*, we may write

$$Al_1 = i_b - i_c \text{ and } Al_2 = i_a - i_d,$$

where i_a, i_b, i_c and i_d represent the enthalpy at various points. For example: let $p_2 = 0.1$ ata and

$$p_1 = 30 \quad 60 \quad 100 \text{ ata}$$
$$\frac{v_d}{v_c} = 0.36 \quad 0.46 \quad 0.55$$
$$Al_1 = 200 \quad 217 \quad 223 \text{ Cal/kg}$$
$$Al_2 = 34 \quad 62 \quad 81 \text{ Cal/kg}$$
$$\frac{l_2}{l_1} = 0.17 \quad 0.29 \quad 0.36$$
$$\eta_t = 0.37 \quad 0.42 \quad 0.45$$

Thus, we see that the relative volume of the compressor is a very considerable value; the work expended on compression is also very great. This, of course, affects the dimensions and cost of the installation but has no negative effect on the theoretical efficiency; the thermal efficiency of the installation, on the contrary, is the higher, the greater the values of $\frac{v_d}{v_c}$ and $\frac{l_2}{l_1}$. In actual practice, however, the use of a compressor of large dimensions has an adverse effect and is uneconomical. This is due to the fact that in a real installation there are a number of losses and harmful resistances, especially friction, connected with the work of driving the compressor, that greatly reduces the effective use of the heat. If we assume that in a real installation the work expended in driving the compressor, $l_2' = 1.5\ l_2$, then, when $p_1 = 100$ ata and $p_2 = 0.1$ ata, we get

$$Al_2' = 1.5 Al_2 = 1.5 \times 81 = 121.5 \text{ Cal/kg}$$

i. e., losses in the compressor are

$$Al_2' - Al_2 = 121.5 - 81 = 40.5 \text{ Cal/kg}.$$

The bigger the compressor, the greater these losses will be. As a result, the work of the installation will be

$$Al' = Al_1 - Al_2' = 223 - 121.5 = 101.5 \text{ Cal/kg}$$

instead of the theoretical

$$Al = Al_1 - Al_2 = 223 - 81 = 142 \text{ Cal/kg},$$

so that the actual use of the heat is expressed by the thermal efficiency

$$\eta_l = \frac{Al'}{Al}\eta_t = \frac{101.5}{142} \times 0.45 = 0.322.$$

If we allow a deviation from the Carnot cycle, that is, change it so that the cumbersome compressor is no longer

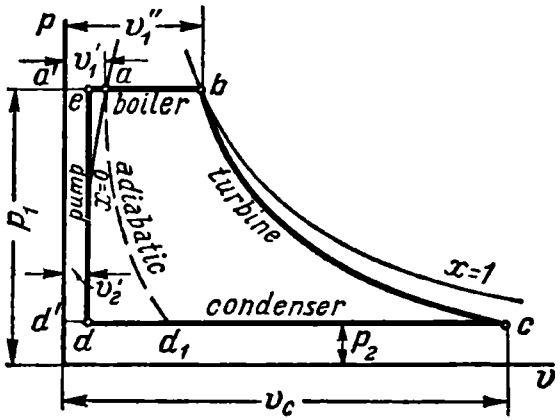


Fig. 13-4

necessary, such an installation, despite the lower efficiency of the cycle, η_l, may make better use of the heat than one working according to the Carnot cycle, to say nothing of its smaller size and lower cost. In the present case a cycle without a compressor whose efficiency is 0.322 would be equal to a Carnot cycle with an efficiency of 0.45.

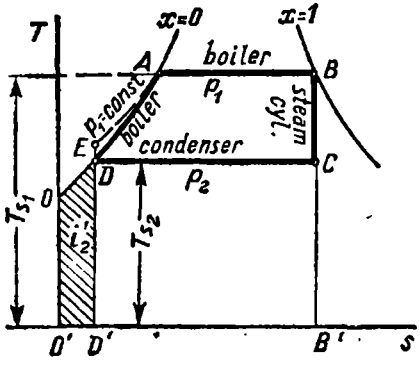


Fig. 13-5

13-2. The Rankine Cycle. The simplest way of getting rid of the compressor without deviating too far from the Carnot cycle is to keep the processes AB and BC of the latter unchanged and continue the isobaric process in the condenser until all the steam has been converted into water at a temperature of T_{s2}; the water is then pumped into the boiler where its temperature is raised to T_{s1} and the cycle is completed (Figs. 13-4 and 13-5).

From the purely theoretical point of view, the water is compressed adiabatically in the pump from pressure p_2 (point D) to pressure p_1, with the results that its specific volume decreases slightly and its temperature is raised (point E). In practice, however, there will be no noticeable error if we consider here to be no change in the volume and temperature of the water after passing through the pump; it will be recalled that for water isobar p_1 merges with the lower threshold curve and point E merges with point D, so that we get the cycle $ABCD$ with the condensate reheated in the boiler from T_{s2} to T_{s1} as represented by the section of the threshold curve DA (Fig. 13-5). In the system pv, the cycle is represented by the figure *eabcd*, in which the isochor *de* represents the passage of the condensate through the pump, and the section of the horizontal line *ea* represents the heating of the condensate in the boiler to boiling point, this section being an isobar and not an isotherm, although section *ab* of the same horizontal, representing the process of steam formation, is both an isobar and an isotherm.

This cycle is known as the *Rankine cycle* and it can be applied in an installation similar to that in Fig. 13-3 by substituting a feed pump for the compressor. Similarly to that of the previous cycle, the area *a'bcd'* (Fig. 13-4) represents the work, l_1, of 1 kg of steam in the cylinder or turbine and area *a'edd'* represents the work of the pump, l_2; l_2 is very small as compared with l_1. Thus, using our former example, i. e., $p_1=100$ ata and $p_2=0.1$ ata, $Al_1=i_b-i_c=$ $=223$ Cal/kg, will still be true, but,

$$Al_2 = A\,(p_1 - p_2)\,v_2' = \frac{(1{,}000{,}000 - 1{,}000)\times 0.001}{427} = 2.34 \text{ Cal/kg}$$

so that the theoretical work of the cycle will be

$$Al = Al_1 - Al_2 = 223 - 2.34 = 220.66 \text{ Cal/kg}.$$

The Carnot cycle under the same conditions gave us $Al=142$ Cal/kg; the Rankine cycle provides a greater amount of work because the work expended on the pump is less than that expended on the compressor in the Carnot cycle. Nevertheless the thermal efficiency of the Rankine cycle is less than that of the Carnot cycle, the latter being the most advantageous within the given temperature limits, because the greater work of the Rankine cycle is connected with a greater expenditure of heat, q_1, on the cycle. In the Carnot

cycle heat is expended only on the formation of steam, so that $q_1 = r_1$, but in the Rankine cycle it is also used to heat the feed-water from T_{s2} to T_{s1}, so that heat is imparted to the working body during processes DA and AB (Fig. 13-5) and is represented by the area $DABB'D'$ which is the difference between area $OABB'O' = i_b$ and area $ODD'O' = i'_2$, i. e.,

$$q_1 = i_b - i'_2,$$

and the work of the cycle is

$$Al = Al_1 - Al_2 = i_b - i_c - A(p_1 - p_2)v'_2,$$

so that the efficiency of the cycle is

$$\eta_t = \frac{Al}{q_1} = \frac{i_b - i_c - A(p_1 - p_2)v'_2}{i_b - i'_2}.$$

Applying this to our example we get

$$\eta_t = \frac{233 - 2.34}{651.7 - 45.4} = 0.37$$

as compared with the 0.45 of the Carnot cycle; if we take into consideration the losses in the pump which amount to

$$Al'_2 = 1.5\, Al_2 = 1.5 \times 2.34 = 3.51 \text{ Cal/kg}$$

and, therefore,

$$Al' = Al_1 - Al'_2 = 223 - 3.51 = 219.49 \text{ Cal/kg},$$

the real efficiency of the cycle will be

$$\eta_t = \frac{Al'}{Al}\ \eta_t = \frac{219.49}{220.66} \times 0.37 = 0.368$$

as compared with 0.322 for the Carnot cycle, i. e., the Rankine cycle is more economical than the Carnot cycle. Furthermore, the installation is more compact and cheaper because the feed pump is much smaller than the compressor—in our example $\frac{v_A}{v_c} = 0.0001$ for the Rankine cycle as compared with 0.55 for the Carnot cycle; for every kg of steam we get 101.5 Cal/kg of useful work in the Carnot cycle and 219.49 Cal/kg in the Rankine cycle so that if the two installations are of equal power the Rankine cylinder will be $\frac{219.49}{101.5} = 2.2$ times smaller than the Carnot cylinder.

Thus, the use of the Rankine cycle in place of the Carnot cycle increases the actual use of the heat and reduces the

dimensions of the installation and, therefore, its weight and cost.

Since the nature of the working substance does not affect the efficiency of the Carnot cycle, superheated steam, theoretically speaking, possesses no advantages over saturated steam; in the Rankine cycle superheated steam gives a somewhat higher thermal efficiency as can be seen from Fig. 13-6.

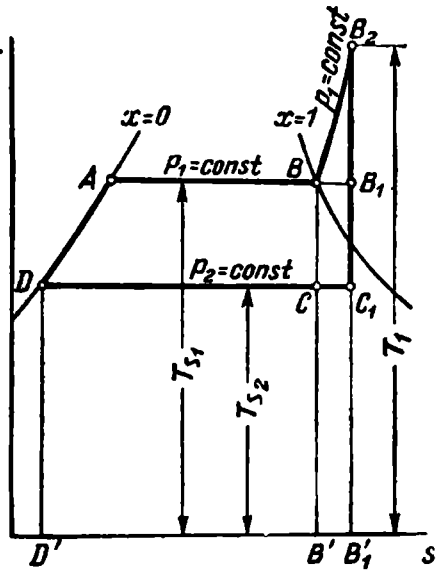


Fig. 13-6

By superheating the steam at constant temperature T_{s1}, (section of the isotherm BB_1) we get the cycle AB_1C_1D within the same temperature limits T_{s1} and T_{s2} of the saturated steam as those used in cycle $ABCD$. The cycle AB_1C_1D may be regarded as consisting of the cycles $ABCD$ and BB_1C_1C; the efficiency, η_t, of the former is less than that of a Carnot cycle for which $\eta_{tc}=1-\frac{T_{s2}}{T_{s1}}$; the latter, being a Carnot cycle, has the efficiency η_{tc}; the efficiency η_{t1} of the total cycle AB_1C_1D will have an intermediate value, i. e.,

$$\eta_{tc} > \eta_{t1} > \eta_t,$$

in other words, the cycle AB_1C_1D is more economical than cycle $ABCD$. Still greater economy can be effected by superheating the steam, not at constant temperature T_{s1}, but at constant pressure p_1, along isobar BB_2, which is usually done in practice.

The efficiency of cycle ABB_2C_1D is greater than that of cycle AB_1C_1D as follows from the general expression for the efficiency of any cycle,

$$\eta_t = 1 - \frac{q_2}{q_1},$$

where q_1 — the amount of heat imparted to the body;
q_2 — the amount of heat given up by the body.

From Fig. 13-6 we see that the value of q_2, represented by area $DC_1B_1'D'$ is the same for both cycles, and the q_1 of cycle ABB_2C_1D, represented by area $DABB_2B_1'D'$ is greater by area BB_2B_1 than that of cycle AB_1C_1D, represented by area $DAB_1B_1'D'$, i. e.,

$$\eta_{t2} > \eta_{t1} > \eta_t.$$

This is only natural because the superheating of the steam along isobar BB_2 raises the higher limit of the temperature of the cycle from T_{s1} to T_1.

Using the data of our last example, i. e., $p_1=100$ ata, $p_2=0.1$ ata and $t_1=450°$ C, we get $\eta_t=0.4$ for superheated steam using the Rankine cycle as compared with 0.37 for saturated steam. In real processes the increased efficiency resulting from superheating is much greater than the theoretically determined increase in thermal efficiency.

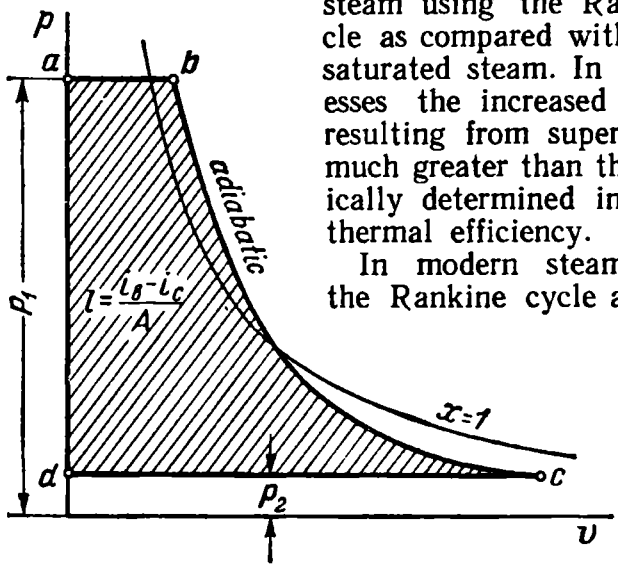


Fig. 13-7

In modern steam engines the Rankine cycle applied to superheated steam at constant pressure is used; the process BB_2 takes place in the superheater and the expansion B_2C_1 in the steam engine or turbine.

We know that in practice the upper threshold curve of water ($x=0$) merges with the axis of the ordinate in the system pv, so that the cycle is represented in this system as the figure *abcd* (Fig. 13-7) which is the same shape as that of the indicator diagram of the steam-engine cylinder for $G=1$ kg, although there is some difference in the meaning of the two figures. From Fig. 13-7 we see that the work of the cycle is equal to the available work obtained from the adiabatic expansion *bc*, and for 1 kg of steam is

$$Al = i_b - i_c; \tag{13-1}$$

the work of the pump, on account of its insignificant value, is ignored. The work of the cycle, Al, is in this case the same as that shown by the indicator diagram of the steam-engine cylinder, or as that of a turbine; this is quite understandable because the work is performed in them and is not expended on the installation (the work of the pump is $Al_2 \approx 0$). The equality of the indicator work and the available work of streaming is to be explained by the fact that the passage of steam through a cylinder may be regarded as a process of streaming from the steam boiler at pressure p_1 into a condenser with a pressure of p_2; the available work is not used to increase the velocity of the steam but is transmitted directly to the piston and expended on the external work of overcoming the resistance on the shaft of the engine. In turbines, the drop in heat is transformed by the nozzles into available work in the form of the kinetic energy of the steam which is then converted into work on the shaft after passing through the blades of the rotor.

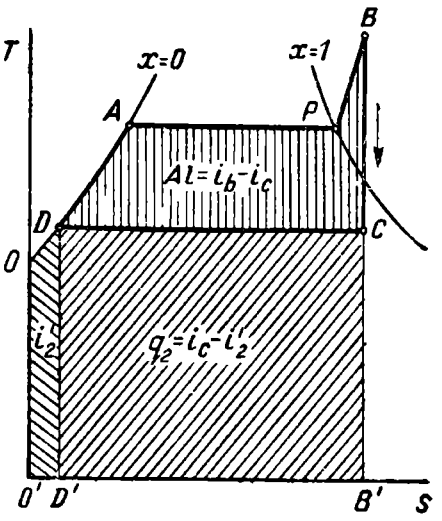


Fig. 13-8

The steam that is brought to the steam engine or turbine from the boiler with a heat content (enthalpy) of i_b is returned to the boiler via the pump with an enthalpy of i'_2 (point D, Fig. 13-8); the amount of heat expended on the conversion of each kilogram into steam in the state indicated by point B is

$$q_1 = i_b - i'_2,$$

so that the efficiency of the cycle is

$$\eta_t = \frac{Al}{q_1} = \frac{i_b - i_c}{i_b - i_2} = \frac{h}{i_b - i_2}, \tag{13-2}$$

where $h = i_b - i_c$, the adiabatic heat drop.

13-3. The Specific Consumption of Steam and Heat. The Relative Internal Efficiency of the Engine. Other values that determine the character of the theoretical use of heat in steam engines and turbines are the *specific consumption of steam* and the *specific consumption of heat*. By the first we mean the quantity of steam in kg consumed by 1 hp-hr or 1 kwh; by the second we mean the amount of heat consumed by the steam required for 1 hp-hr or 1 kwh.

Since 1 hp-hr=632 Cal and 1 kwh=860 Cal, the work of 1 kg of steam in the Rankine cycle is, theoretically,

$$Al = i_b - i_c = h,$$

so that the specific consumption of steam (theoretically) is

$$d_t = \frac{632}{Al} = \frac{632}{h} \text{ kg-hp-hr} \qquad (13\text{-}3)$$

or

$$d_t = \frac{860}{Al} = \frac{860}{h} \text{ kg-kwh} \qquad (13\text{-}4)$$

where h—the adiabatic heat drop.

The heat consumed on every kilogram of steam in the Rankine cycle is

$$q_1 = i_b - i_2'';$$

therefore, the specific consumption of heat on 1 hp-hr or on 1 kwh, on which d_t kilograms of steam is consumed, is, including equation 13-2 in the calculation,

$$W_t = q_1 d_t = (i_b - i_2'')\frac{632}{h} = \frac{632}{\eta_t} \text{Cal per hp-hr,} \qquad (13\text{-}5)$$

or

$$W_t = \frac{860}{\eta_t} \text{Cal per kwh.} \qquad (13\text{-}6)$$

Thus, we see that η_t and W_t determine each other. The specific consumption of heat, W_t, therefore, is sufficient to give a full characteristic of the economic functioning of the cycle.

The specific consumption of steam, d_t, is a different matter, as can be seen, for example, from the relation

$$\eta_t = \frac{632}{W_t} = \frac{632}{q_1 d_t}.$$

With one and the same d_t and, therefore, one and the same h (equation 13-3), the thermal efficiency, η_t, will vary depending on the value of $q_1 = i_b - i'_2$; in other words, the specific consumption of steam d_t does not, by itself, determine the degree of economy in the functioning of the cycle, i. e., it is not sufficient to determine its efficiency, η_t. If we compare the following:

p_1	t_1	p_2	h	i_b	i'_2	q_1	d_t	η_t
10	320	1	115	738.4	99.2	639.2	5.5	0.180
18	230	1.2	115	683.3	104.38	578.92	5.5	0.198,

we see that although the specific consumption of steam, d_t, is the same in each case, the second cycle is the more economical.

As we have seen, the thermal efficiency, η_t, of the cycle takes into consideration only one loss, that of the waste heat, q_2. Actually to this must be added a number of other losses in the cylinder of the engine or the housing of the turbine, losses that reduce the work of the steam in the engine; these losses constitute the *internal work* l_i. The relation

$$\eta_{0i} = \frac{l_i}{l} = \frac{Al_i}{h} \qquad (13\text{-}7)$$

takes these additional losses into consideration; they are the reason for a real steam process in an engine or turbine deviating from the theoretical; η_{0i} is the *relative internal efficiency* of the machine.

The real use of the heat, q_1, that is imparted to the steam in the boiler, is calculated similarly to that of the theoretical when it is transformed into work, by the relation

$$\eta_i = \frac{Al_i}{h} \qquad (13\text{-}8)$$

which is known as the *absolute internal efficiency* of the machine; it takes into consideration both the loss, q_2, and the additional losses inside the machine. It will easily be seen that

$$\eta_i = \frac{Al_i}{q_1} = \frac{l_i}{l} \times \frac{Al}{q_1} = \eta_{0i}\eta_t. \qquad (13\text{-}9)$$

Obviously it is the absolute internal efficiency, η_i, that is of practical interest and not the efficiency of the cycle, η_t.

Example 13-1. Determine the efficiency η_t of a Rankine cycle employing superheated steam at $p_1=10$ ata, $t_1=350°$ C and $p_2=0.1$ ata and also the specific consumption of heat and steam in the theoretical process.

From the *is* graph we find that

$$i_b=754 \text{ Cal/kg and } h=i_b-i_c=202 \text{ Cal/kg,}$$

so that, applying equation 13-2

$$\eta_t=\frac{i_b-i_c}{i_b-i_2'}=\frac{202}{754-45.4}=\frac{202}{709.6}=0.285.$$

The theoretical specific consumption of heat in the steam for one hp-hr is

$$W_t=\frac{632}{\eta_t}=\frac{632}{0.285}=2{,}220 \text{ Cal per hp-hr,}$$

and the consumption of steam is

$$d_t=\frac{632}{Al}=\frac{632}{h}=\frac{632}{202}=3.13 \text{ kg per hp-hr.}$$

If working with dry saturated steam without superheating we should have

$$i_b=663 \text{ Cal/kg; } i_b-i_c=166 \text{ Cal/kg;}$$

$$\eta_t=\frac{166}{663-45.4}=\frac{166}{617.6}=0.268;$$

$$W_t=\frac{632}{0.268}=2{,}360 \text{ Cal per hp-hr;}$$

and

$$d_t=\frac{632}{166}=3.8 \text{ kg per hp-hr.}$$

For a Carnot cycle employing dry saturated steam:

$$\eta_t=1-\frac{T_{s2}}{T_{s1}}=1-\frac{273+45.45}{273+179.04}=0.295,$$

$$Al=\eta_t q_1=\eta_t r_1=0.295\times 482.1=142.5 \text{ Cal/kg,}$$

$$W_t=\frac{632}{0.295}=2{,}140 \text{ Cal per hp-hr and } d_t=\frac{632}{142.5}=4.44. \text{ kg per hp-hr}$$

Thus, we see that the greatest consumption of steam takes place when the Carnot cycle is used despite the fact that this is the most economical cycle, as the figures for the specific consumption of heat show. Here we have proof of the fact that the specific consumption of steam cannot alone be used as an index of efficiency.

13-4. Methods of Improving the Efficiency of a Steam Cycle.

From equation 13-2,

$$\eta_t=\frac{i_b-i_c}{i_b-i_2'}=\frac{h}{i_b-i_2'},$$

we see that the efficiency, η_t, depends on three values: i_b, i_c, i'_2. The enthalpy of the fresh steam, i_b, is determined by its pressure p_1 and temperature t_1; the enthalpy of the feed-water, i'_2, is determined by the pressure, p_2, at the end of the expansion (the pressure in the condenser); the parameters p_1, t_1 and p_2 give the enthalpy of the steam, i_c, at the end of the adiabatic expansion. Thus, the efficiency, η_t, is fully determined by the parameters p_1, t_1 and p_2. We shall now see how they affect the efficiency, η_t, and what ways there are of raising it.

Let us first study the effect of the initial pressure, p_1. We can see from the *is* diagram (Fig. 13-9) that by increasing the initial pressure, p_1, at constant t_1 and p_2 we can reduce the enthalpy of the fresh steam, i_b, and at the same time increase the temperature drop h with the result that the efficiency, η_t, is raised.

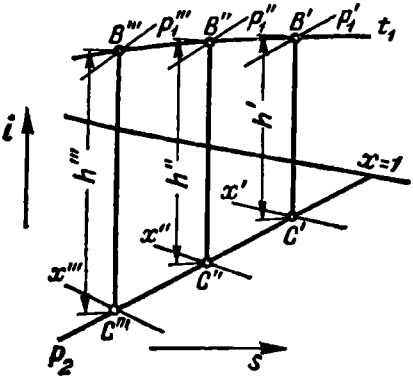


Fig. 13-9

Using superheated steam at $t_1=400°C$ and pressure in the condenser, $p_2=0.04$ ata, we get the following:

$$p_1 = 30 \quad 30 \quad 60 \quad 100 \text{ ata}$$
$$\eta_t = 34.9\% \quad 36.7\% \quad 39.4\% \quad 41.2\%.$$

These figures explain why the development of steam engines has always been connected with increased boiler pressures.

This fact is very clearly seen in the development of power engineering in the Soviet Union. Power engineering began to develop rapidly shortly after the October Revolution, and the new thermal power stations were designed for increasing steam pressures. Lenin's famous plan for the electrification of Russia (the GOELRO plan) adopted in December 1920 envisaged the building of thermal power stations that, in the majority of cases, were calculated to work at a pressure of 20 ata; by the time of the First Five-Year Plan (1928-1932) the most widespread type of steam-driven plant was working at pressures between 30 and 37 ata. In the prewar years most of the stations went over to a standard pres-

sure of 31.5 ata, but a number of high-pressure installations were built to work at pressures ranging from 60 to 140 ata.

After the Second World War, however, Soviet power engineers began to make use of very high steam pressures. A large number of power plants working at a pressure of 100 ata have been built during the past few years. Some installations have been designed to work at 170 ata and more; there are also experimental boiler-turbine units working at a pressure of 300 ata.

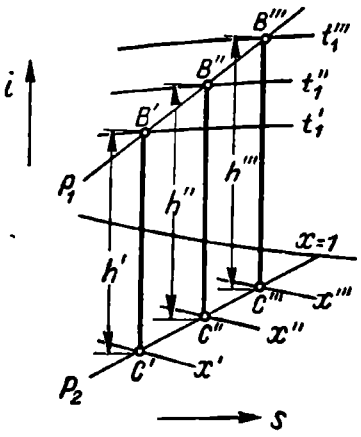


Fig. 13-10

An adverse effect resulting from increased initial pressure is the greater amount of moisture in the steam at the end of expansion as can be seen from the *is* diagram given in Fig. 13-9 where $p'''_1 > p''_1 > p'_1$ and simultaneously $x''' < x'' < x'$; this lower quality of the steam means increased losses in the turbine which affect the efficiency, η_{oi} thus reducing the actual use of the heat on which efficiency η_i is based. Thus, the raising of the boiler pressure and of the thermal efficiency, η_t, of the Rankine cycle may lead to a less economical working of the installation on account of the great humidity at the end of the expansion. Another thing of great importance—extreme humidity at the end of the expansion (greater than 12%) leads to serious wear and tear on the turbine blades.

The humidity of the steam at the end of the expansion may be reduced by increasing the superheat, t_1, as can be seen from the *is* diagram in Fig. 13-10 where $t'''_1 > t''_1 > t'_1$ so that $x''' > x'' > x'$. It is, therefore, only natural that an increase in boiler pressure must be accompanied by superheating at a higher t_1. The increase of t_1, at constant p_1 and p_2, as the higher temperature in the cycle, raises the efficiency η_t of the cycle, but not to a very great extent, because the increased heat drop, h, is accompanied by greater enthalpy, i_b. Thus, for $p_1 = 25$ ata and $p_2 = 0.04$ ata we get the following:

$t_1 =$	300	350	400	450	500	550	600°C
$\eta_t =$	35.2	35.6	36.2	37.0	37.6	38.4	39.2%.

The actual economy effected by the use of greatly superheated steam is much higher than the theoretical economy.

The history of the development of power engineering is one of increasing pressures and steam temperatures. The GOELRO plan (1920) envisaged thermal power stations working on superheated steam at 375°C, but at the time of the First Five-Year Plan (1928-1932) a number of steam-driven stations were working at temperatures in the 400°-450°C

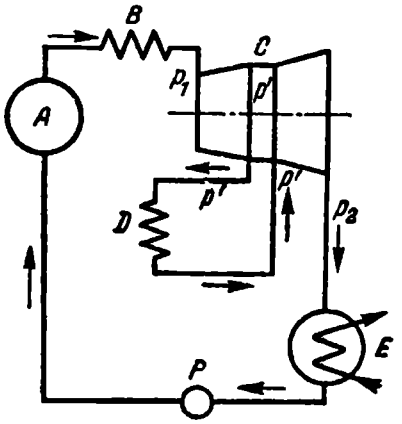


Fig. 13-11

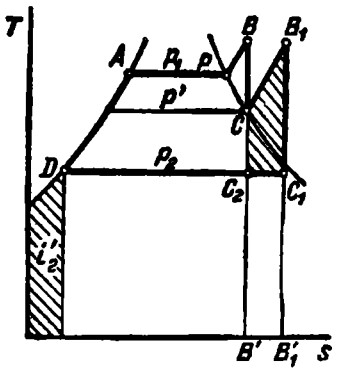


Fig. 13-12

range. A heat and power station opened in Moscow in 1933 was designed to work at a pressure of 140 ata and a temperature of 500°C.

Since the war the use of steam at 100 ata and 500°C has been almost universally introduced; industrial power stations work at 550°C and there are some experimental installations that work at 600°C.

One of the methods by which power installations are made more economical is that of *secondary superheating* which reduces the moisture when the steam is discharged from the turbine. The steam, reduced to a saturated state as it leaves the turbine, passes into a special superheater from which it is returned to the turbine and continues its expansion to pressure p_2 in the condenser.

A schematic diagram of an installation employing secondary superheating is given in Fig. 13-11: *A* is the boiler; *B*, the first superheater; *C*, the turbine; *D*, the second superheater; *E*, the condenser and *H*, the pump.

The second superheating naturally changes the steam cycle; the new cycle is shown in Fig. 13-12 in a *Ts* system as the area $APBCB_1C_1D$, the section of the isobar CB_1, representing the secondary superheating at constant pressure, p'. If there were no secondary superheating the cycle would be $APBC_2D$; the secondary superheating reduces the humidity at the end of the expansion ($x_{c_1} > x_{c_2}$) and increases the heat drop by the shaded area $CB_1C_1C_2$ at the cost of an additional consumption of heat in the second superheater which is equal to the area $CB_1B_1'B'$. The efficiency of the cycle $APBCB_1C_1D$ is,

$$\eta_t = \frac{i_b - i_c + i_{b1} - i_{c1}}{i_b - i_2' + i_{b1} - i_c}, \qquad (13\text{-}10)$$

while that of cycle $APBC_2D$, without secondary superheating is

$$\eta_t' = \frac{i_b - i_{c2}}{i_b - i_2'}. \qquad (13\text{-}11)$$

It is possible, by an approximate calculation, to establish the fact that the efficiency, η_t, may be higher, equal to or lower than η_t', depending on the pressure p' chosen for the second superheater, i. e., secondary superheating may even cause a poorer theoretical use of heat, as can be seen from Fig. 13-13. For each individual case p' has a specific value that corresponds to maximum η_t. Belated superheating is uneconomical because the heat employed for the second superheater is scarcely used by the turbine but is transmitted to the condenser.

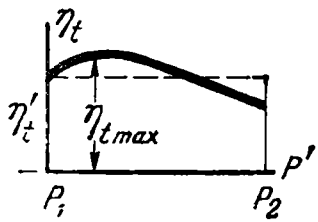


Fig. 13-13

In general, the theoretical economy of secondary superheating is not very great, but in actual practice there is greater economy because secondary superheating reduces the moisture at the end of the expansion which decreases losses in the stages of the turbine. When secondary superheating is used, moisture at the end of the expansion reaches the figure of 8%, being the higher, all other conditions being equal, the greater the initial pressure p_1, the latter giving greater moisture at the end of expansion if there is no secondary superheating. In addition to the more economical

use of heat, secondary superheating gives longer life to the turbine blades.

A very effective method of raising the thermal efficiency, η_t, is the reduction of the final pressure of expansion, p_2. For example, at $p_1=30$ ata and $t_1=400°C$ we get for

$$\begin{array}{lccccccc} p_2= & 1 & 0.1 & 0.08 & 0.06 & 0.04 & 0.02 \text{ ata} \\ \eta_t= & 25.5 & 33.9 & 34.7 & 35.5 & 36.7 & 38.5\%. \end{array}$$

The reduction of pressure p_2, the pressure of the steam when it leaves the turbine or engine, to a value below that of one atmosphere, is effected by an artificial vacuum maintained in the condenser due to the steam giving up heat to the coolant and condensing. In general, the temperature of the condensate and, therefore, the pressure in the condenser, is the lower, the lower the temperature of the cooling water and the greater the *cooling factor*, i. e., the weight of cooling water expended on 1 kg of steam. With the water at a given temperature, a reduction in the cooling time will, in general, produce a lower p_2 and a higher η_t, but this also involves an increased expenditure of energy on the pump that drives the circulating water through the condenser. There is, therefore, an economically advantageous degree of vacuum for each separate case which, in turbine installations, does not exceed 96% ($p_2=0.04$ ata).

The work of a steam engine without a condenser, i. e., when the exhaust steam is ejected into the atmosphere ($p_2 \approx 1$ ata), as most locomotives work, is very uneconomical; for example, when $p_1=16$ ata, $t_1=350°C$ and $p_2=1$ ata, the efficiency η_t will be 21.2% whereas with the same initial parameters and $p_2=0.1$ ata, the efficiency would be 33.3%. High vacuum in a modern locomotive is practically impossible because the cylinders of the condenser, even for a 90% vacuum, would be too clumsy; on account of the high specific volume of the steam at low pressures, they cannot be reduced to the required dimensions. High vacuums could be used on a locomotive only if the reciprocating engine were replaced by the more compact turbine. A number of turbine locomotives have been designed but owing to their intricacy and, therefore, unreliability in exploitation, have not found widespread favour.

Since the steam locomotive is an uneconomical machine, the production of them has ceased completely in the U.S.S.R.

It must be mentioned that in those installations in which

the used steam is ejected into the atmosphere and does not return in the form of a condensate to the boiler, and where the boiler is fed with water at a temperature lower than T_{s2}, the cycle is not, strictly speaking, completed. Nevertheless, even in this case it is possible to speak of a cycle if we imagine that the used steam released into the atmosphere condenses and cools to the temperature of the feed-water (point E) along line CDE (Fig. 13-14). In that case we get the cycle $ED'A'P'B'CDE$, during which heat, q_1, imparted to the steam equals the area $EAPBB'E'=i_b-i'$; the amount of heat taken from it is q_2=area $EDCB'E'=i_c-i'$ which performs the work $Al=q_1-q_2=i_b-i_c$=area $APBCD$.

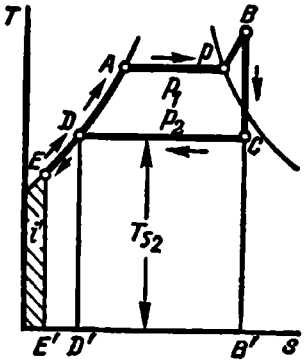


Fig. 13-14

The efficiency of this cycle is

$$\eta_t=\frac{Al}{q_1}=\frac{i_b-i_c}{i_{air}-i'},$$

and it is less than that of the Rankine cycle $APBCD$ because with an equal amount of work for both cycles the consumption of heat in the former is greater than in the latter by the area $EDD'E'=i_2'-i'$. When $p_1=16$ ata, $t_2=350$°C and $p_2=1$ ata, the efficiency of the Rankine cycle is 21.2%, and with the temperature of the feed-water at 15°C, i. e., $i'=15$ Cal/kg, the efficiency η_t is 18.7%.

13-5. The Binary Cycle. The efficiency of the Rankine cycle using superheated steam, as effected in modern steam installations, differs from the Carnot cycle (Sec. 13-2) because it depends not only on the temperature of the fresh steam t_1 but also on its pressure, p_1, i. e., it depends on the temperature of saturation t_{s1} and increases as that temperature increases. This is a confirmation of the basic postulate of thermodynamics which states that heat must be imparted to the working body in a cyclic process at the highest possible temperature; t_{s1} is the temperature at which vapour forms in the boiler. In the case of steam the raising of the temperature t_{s1} is limited by the relatively low critical temperature, i. e., $t_{cr}\approx374$°C, with which is connected a very high critical pressure $p_{cr}\approx225$ ata. At the temperature of the superheated steam $t_1=450$°C, the maximum value of the

temperature of saturation $t_{s1}=t_{cr}=374°C$ and $p_2=0.04$ ata ($t_{s2}=28.6°C$) we get an efficiency of $\eta_t=0.434$; for a Carnot cycle with the same temperature limits, t_1 and t_{s2}, we should get an efficiency of $\eta_{t_c}=0.583$. Thermal efficiency may be raised by substituting some other liquid for water, one that has a higher critical temperature, which would enable the temperature t_{s1} to be raised and bring it closer to t_1, the highest temperature of the cycle. In this respect mercury is the most suitable liquid, since its critical temperature is well over 1000°C and, a very important fact from the practical point of view, the pressures of saturated mercury vapour at high temperatures are not very great; for example, temperature $t_{s1}=450°C$ has a corresponding pressure of p_1 4.5 ata. With temperatures of $t_{s1}=t_1=450°C$ and $t_{s2}=28.6°C$ a saturated mercury vapour cycle with an efficiency of $\eta_t=0.55$ could be obtained as compared with the highest possible efficiency for steam of $\eta_t=0.434$ and a Carnot cycle efficiency of $\eta_{t_c}=0.583$.

The mercury vapour cycle, however, is impossible to achieve in practice because the pressure that corresponds to a temperature of $t_{s2}=28.6°C$ is $p_2=0.00000347$ ata, i. e., an almost perfect vacuum and a correspondingly tremendous volume, so that no installation for its use can be designed. The normal present-day condenser pressure of $p_2=0.04$ ata corresponds to a mercury vapour temperature of $t_{s2}=216.9°C$. But when $t_1=t_{s1}=450°C$, i. e., at a pressure of 4.5 ata, and $p_2=0.04$ ata (at a temperature of $t_{s2}=216.9°C$), the efficiency of the mercury vapour cycle is $\eta_t=0.308$ which is lower than the maximum possible for water vapour, i. e., 0.434 ($p_1=225$ ata, $t_1=450°C$, $p_2=0.04$ ata, $t_{s2}=28.6°C$). The reason for this is the following: at similar initial temperatures of $t_1=450°C$ the lower temperature of the mercury vapour cycle (216.9°C) is much higher than that of the steam cycle (28.6°C). If the t_{s2} of water were as high as 216.9°C (that of mercury vapour) the efficiency of the cycle would be only 0.216.

The mercury vapour cycle has a distinct advantage over steam, therefore, insofar as a temperature drop from 450°C to approximately 200°C is concerned; since there still remains a possible drop to a much lower temperature that is unused it is of advantage to use this for a steam cycle, obtaining the steam during the condensation of used mercury vapour at high temperatures.

Thus, we have an installation working on the vapours of two liquids, mercury and water. This installation employs two cycles, the mercury vapour and steam cycles, or, to use a more scientific term, it employs *a binary cycle.*

A simple schematic diagram of such an installation is given in Fig. 13-15. Fuel is burned in the firebox of the mercury boiler *A* where vapour is formed at low pressure (2-5 ata) and high temperature (400-460°C). This vapour is injected into the mercury vapour turbine *B* where it expands to a pressure of 0.04-0.06 ata and from there passes at a temperature of 220-230°C to the mercury vapour condenser *C* where it is fully condensed and returned to the boiler as liquid mercury. The mercury vapour condenser is cooled by water which is heated to a temperature of 200-210°C at a pressure of 16-20 ata by the heat given up by the mercury; the mercury condenser, therefore, is also a steam boiler heated by the used mercury vapour. The steam is then injected into steam turbine *D* where it expands to a pressure of about 0.04 ata, leaves the turbine at a temperature of about 28°C and passes into the condenser *E* where it is fully condensed and returned to the boiler *C* in the form of feedwater. The diagram shows clearly that two cycles function simultaneously, one employing mercury and the other water.

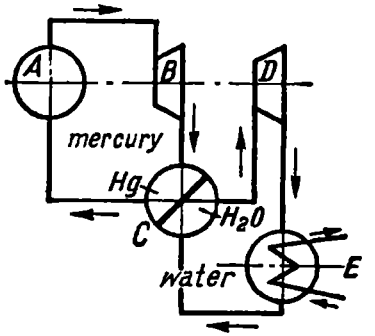


Fig. 13-15

Apart from the higher temperatures, another advantage of mercury in a cyclic process is the low weight heat capacity of liquid mercury which has a mean c' of 0.033, so that a very small amount of heat must be expended to raise the temperature to boiling point. This means that the efficiency of the mercury cycle is close to that of the Carnot cycle; thus, for example, for the Rankine mercury cycle we had at $t_1 = t_{s1} = 450$°C and $t_{s2} = 216.9$°C an efficiency of $\eta_t = 0.308$ while the corresponding efficiency of the Carnot cycle would be $\eta_{t_c} = 0.323$; therefore $\frac{\eta_t}{\eta_{t_c}} = \frac{0.308}{0.323} = 0.953$. The heat capacity of water is $c \approx 1$, i. e., 30 times greater than that of mercury, so that the Rankine steam cycle differs from the Carnot

cycle to a greater degree, i. e., $\frac{\eta_t}{\eta_{t_0}}=0.8$ to 0.9. On the other hand, the relatively small heat of steam formation of mercury is unfavourable; it is approximately $t_s=216.9°C$, $r=71.62$ Cal/kg and, therefore, the mercury vapour has a low enthalpy, at $p=4.5$ ata it is only $i''=85$ Cal/kg while that of steam at the same pressure is $i''=655.2$ Cal/kg. This low enthalpy conditions low heat drops and a big specific consumption of mercury vapour.

If l_m—the work of 1 kg mercury vapour for the cycle;
l_w—the work of 1 kg steam for the cycle;
q_{1m}—the amount of heat imparted to 1 kg vapour in the mercury boiler;
q_{1w}—the amount of heat imparted to 1 kg steam in the water boiler;
q_{2m}—the heat given up by 1 kg mercury vapour in the mercury condenser;
η_{t_m}—the thermal efficiency of the mercury cycle;
η_{t_w}—the thermal efficiency of the water cycle;
G—the amount of mercury by weight necessary to obtain 1 kg of steam,

the total thermal efficiency of the cycle, i. e., the thermal efficiency of the binary cycle, in which 1 kg of steam and G kg of mercury vapour are used, is determined by the relation of the total work of the cycle which is $AL=GAl_m+Al_w$ to the consumption of heat $Q_1=Gq_{1m}$, because heat is expended only on the mercury cycle to obtain the work of the steam cycle. Therefore,

$$\eta_t=\frac{AL}{Q_1}=\frac{GAl_m+Al_w}{Gq_{1m}}=\frac{Al_m}{q_{1m}}+\frac{Al_w}{Gq_{1m}}. \qquad (13\text{-}12)$$

The thermal efficiencies of the mercury and water cycles are respectively

$$\eta_{t_m}=\frac{Al_m}{q_{1m}}=1-\frac{q_{2m}}{q_{1m}} \text{ and } \eta_{t_w}=\frac{Al_w}{q_{1w}}$$

so that

$$q_{1w}=Gq_{2m}$$

and, therefore,

$$Al_w=\eta_{t_w}q_{1w}=\eta_{t_w}Gq_{2m}.$$

Making the necessary substitutions, we get the efficiency of the binary cycle as

$$\eta_t=\eta_{t_m}+\eta_{t_w}\frac{q_{2m}}{q_{1m}},$$

and since $\frac{q_{2m}}{q_{1m}} = 1 - \eta_{t_m}$ we get the final equation

$$\eta_t = \eta_{t_m} + \eta_{t_w}(1 - \eta_{t_m}) = \eta_{t_m} + \eta_{t_w} - \eta_{t_m}\eta_{t_w}. \quad (13\text{-}13)$$

For example: working with saturated mercury vapour at pressure $p_{1m}=4.5$ ata ($t_{s1m}=450$°C), expanding to pressure $p_{2m}=0.04$ ata ($t_{s2m}=216.9$°C), $Al_m=24$ Cal/kg, $i''_{1m}=85.02$ Cal/kg and $i'_{2m}=7.16$ Cal/kg, the efficiency of the mercury cycle will be:

$$\eta_{t_m} = \frac{Al_m}{i''_{1m} - i'_{2m}} = \frac{24}{85.02 - 7.16} = 0.308.$$

A certain drop in temperature will be necessary in the mercury condenser to transfer the heat from the mercury to the water; assuming it to be 16.5°C, the temperature of the saturated water vapour will be 216.9—16.5=200.4°C corresponding to which we get a steam pressure of $p_{1w}=16$ ata. The work derived from the expansion of the steam to pressure $p_{2w}=0.04$ ata will be

$Al_w = 205.5$ Cal/kg; $i''_{1w} = 667.1$ Cal/kg; $i'_{2w} = 28.641$ Cal/kg;

and the efficiency of the water cycle is

$$\eta_{t_w} = \frac{Al_w}{i''_{1w} - i'_{2w}} = \frac{205.5}{667.1 - 28.641} = 0.322$$

and, consequently, the efficiency of the binary cycle

$$\eta_t = 0.308 + 0.322 - 0.308 \times 0.322 = 0.53$$

as compared with the maximum possible within the same temperature limits for a Rankine steam cycle, i. e., 0.434 and with the efficiency of a Carnot cycle, i. e., 0.583. Thus, we see that the effect of the use of mercury in a binary cycle is very great. The practical advantage of the binary cycle has been proved on a number of installations of 10,000-20,000 kw. In an actual installation the steam leaves the mercury condenser superheated to 400-450°C which reduces the losses in the turbine and protects the turbine blades from corrosion due to moisture. The use of superheated steam reduces the efficiency of the binary cycle, although the reduction is a very slight one.

The obstacles in the way of the more widespread use of mercury are the high cost of the mercury itself (it is needed in very large quantities in powerful installations) and the poisonous nature of mercury vapour. In our example, to

obtain 1 kg of steam it is necessary to use

$$G=\frac{q_{1w}}{q_{2m}}=\frac{i''_{1w}-i'_{2w}}{i_{2m}-i'_{2m}}=\frac{667.1-28.641}{61-7.16}=11.85 \text{ kg},$$

i. e., almost 12 kg of mercury vapour per kg of steam.

Research institutions are carrying out experiments for the purpose of substituting other bodies with a high boiling point for mercury such as diphenyl, hydrocarbons, aluminium bromide, etc., but so far no results of practical value have been obtained.

In Fig. 13-16, the two cycles, mercury and water, are shown diagrammatically in a coordinate system Ts; the water cycle $A_2B_2C_2D_2$ is for 1 kg, as usual, and the mercury cycle $A_1B_1C_1D_1$ is for $G=11.85$ kg. In conformity with this the water threshold curves are for 1 kg and the mercury threshold curves for 11.85 kg of vapour. Since liquid mercury has a low weight heat capacity, the threshold curve $x=0$ rises very sharply to the right making the figure $A_1B_1C_1D_1$ for mercury close in shape to a rectangle, i. e., close to the Carnot cycle, which cannot be said of the steam cycle $A_2B_2C_2D_2$.

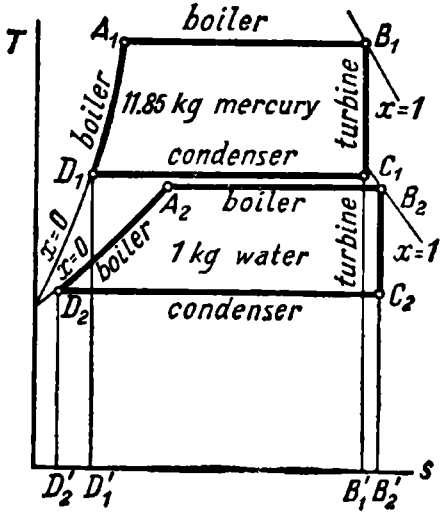


Fig. 13-16

The theoretical work of 1 kg of steam in the turbine is $Al_w=205.5$ Cal/kg; the simultaneous work of 11.85 kg of mercury vapour in the mercury turbine is $GAl_m=11.85\times\times24=284$ Cal. The total work of the two turbines is $AL=284+205.5=489.5$ Cal, so that the mercury turbine accounts for $\frac{284}{489.5}\times100=58\%$ of the capacity of the installation and the steam turbine for 42%.

13-6. The Compound Use of Heat. The Fundamentals of Heat Supply. As we have seen in the previous chapters, the thermal efficiency of a steam cycle can, at the best, only reach something like 50%. This means that in the

very best case, when the losses in the boiler and turbine are taken as zero, half the heat generated by the combustion of fuel is lost.

Real losses are even greater. If the thermal efficiency of a power installation is 50% its real efficiency is, at the best, about 35%. Fig. 13-17 represents the heat balance of a power

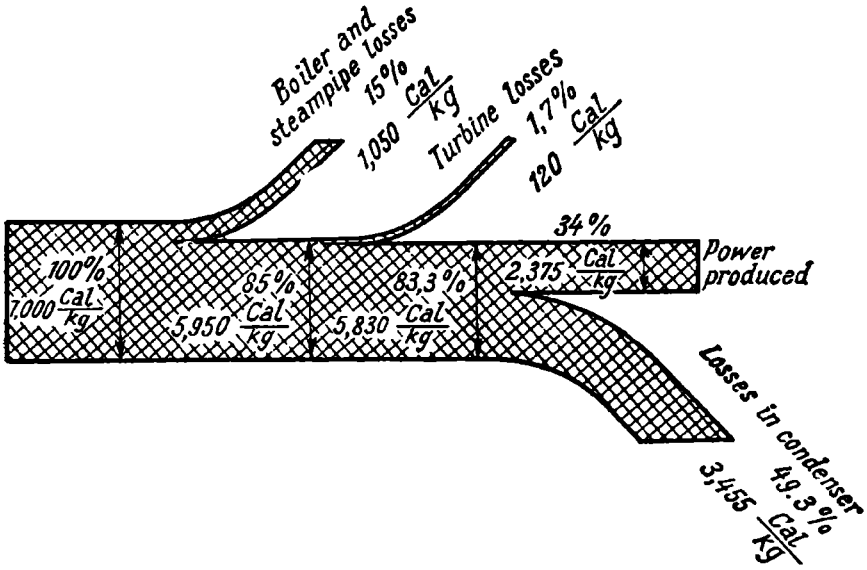


Fig. 13-17

plant employing condensation. The heat generated as a result of firing 1 kg of conventional fuel (i. e., fuel capable of generating 7,000 Cal/kg) is taken as 100%. The first losses are in the boiler installation: part of the heat is carried away by the chimney gases whose temperature is always higher than that of the atmosphere; more heat is lost as a result of the incomplete chemical combustion of the fuel; part is absorbed by the boiler and transmitted to the surrounding medium. If we add to boiler losses those of the steampipe conducting the steam to the turbine, the efficiency of the boiler may be taken as a maximum of 0.85. Therefore the losses in the boiler and steampipe amount to $7{,}000(1-0.85)=1{,}050$ Cal per kg of conventional fuel, or 15%. The losses in the turbogenerator are not high. In our Fig. 13-17 these losses are estimated at 1.7%, i. e., about 120 Cal per kg of fuel. These low losses are explained by the fact that the steam turbine and power generator are highly

perfected machines with a very high efficiency; furthermore, the heat imparted to the turbine and not converted into work is not irretrievably lost but increases the enthalpy of the steam leaving the turbine. The imperfect work of a steam turbine, therefore, increases the condenser losses.

In Fig. 13-17 the condenser losses are estimated at 49.3% and constitute about 3,455 Cal per kg of conventional fuel. These losses are determined in the first place by the value of the thermal efficiency of the cycle * and, secondly, by the efficiency of the turbine. Thus, only about 34% of the heat generated by the combustion of 1 kg of conventional fuel, or about 2,375 Cal per kg, can be converted into electrical energy.

It will be seen from the heat balance in Fig. 13-17 that the greater part of the heat (about a half) is lost in the condenser cooling water. A substantial reduction in these losses can be effected in only one way—by raising the thermal efficiency of the cycle. But, as we have seen, this is no simple matter since a *substantial* increase in the thermal efficiency requires a very considerable increase in the higher heat reservoir or a considerable lowering of the temperature of the cold reservoir.

The temperature of the cold reservoir is determined by the temperature of the cooling water; in this sphere possibilities are limited. The temperature of the higher heat reservoir may be raised by using steam with a high degree of superheat at high pressures. This latter method, therefore, is that adopted for the development of Soviet power engineering, as we said above.

The use of superheated steam at very high temperatures and pressures is made difficult by the necessity to find materials for boiler and turbine construction that will withstand the high temperatures under pressure, so that in this field the limits are set by the metallurgists.

The use of steam at super-high temperatures and pressures, however, does not do away with the heat losses (over 50%) during the combustion of fuel and so ways are being sought to use more economically the reserves of fuel that have been hidden in the earth for many millions of years.

* It must be borne in mind that the theoretical losses determined by the value of η_t do not refer to the total heating capacity of the fuel; a reduction must be made for boiler and steampipe losses, i. e., in the given case, they do not refer to 7,000 Cal but to 7,000—1,050=5,950 Cal.—*Ed.*

Society needs electricity and heat, and fuel must be expended to obtain them. Heat is necessary for technical purposes and to heat houses and supply the population with hot water. Heat is usually transmitted as saturated (or slightly superheated) steam at pressures between 1.5 and 7 atm gauge, or as hot water at temperatures ranging from 50°C to 120°C.

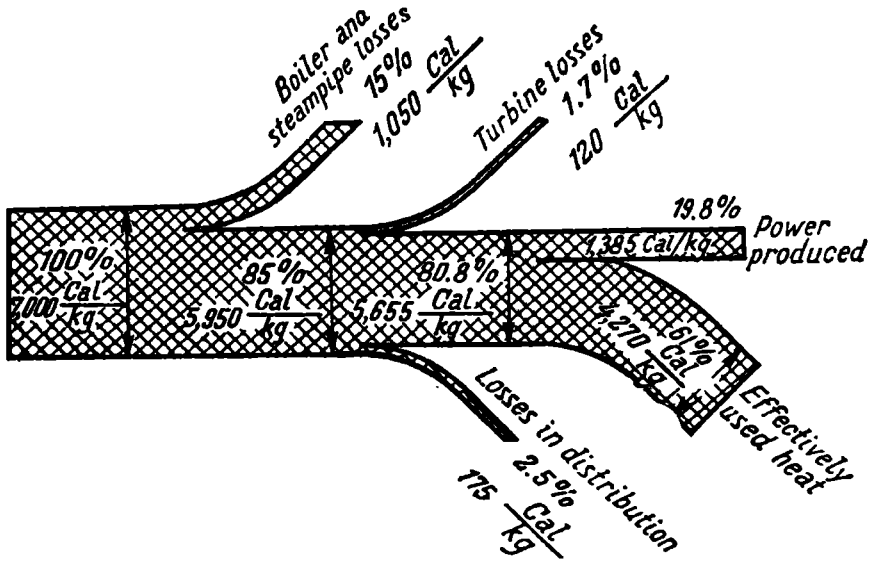


Fig. 13-18

If the engineer tries to achieve the greatest efficiency in his power installation, the heat transmitted to the cooling water in the condenser cannot be used for either industrial or domestic purposes because of its low temperature. A more economical use of fuel is provided by combined power and heating systems; the pressure, p_2, of the steam may be raised when it leaves the turbine and this will raise the temperature of the coolant which may be used in heating systems (where such heating is used) or the counterpressure may be raised and the steam from the turbine sent, for example, to a factory for technical purposes.

This measure will, of course, reduce the amount of work obtained from each kilogram of fuel, but the heat that would otherwise be thrown away with the cooling water will be used. This solution to the problem is of great interest and importance.

We now come to the *combined* use of the energy of heat in power production. Fig. 13-18 shows the heat balance of what is known in the Soviet Union as a "*heat and power station*", that is, an electric power station that supplies electric energy and also heat for industrial and domestic use. As in the previous diagram, we take the heat generated by 1 kg of conventional fuel, i. e., 7,000 Cal, as 100%. The efficiency of the boiler and steampipe is taken as 85%, as in the previous example. The losses in this part of the installation will be, as before, 1,050 Cal per kg of fuel—i. e., 15%. We may assume that the turbine losses also remain unchanged at 1.7%, i. e., 120 Cal per kg of fuel. In this case, however, we have to consider another inevitable loss, that of the heat network, which may be taken as approximately 2.5% or 175 Cal. The remaining heat, 80.8%, or 5,655 Cal per kg of conventional fuel, may be utilised. Part of this heat is used directly for the production of electric power, and the other part (which is considerably greater) is sent to the heat user. Fig. 13-18 shows that only 1,385 Cal or 19.8% of the heat is converted into electric power and that 61% or 4,270 Cal of the heat generated by the combustion of 1 kg of conventional fuel is transmitted to heat users.This is the system of communal domestic heating now employed by many Soviet power stations.

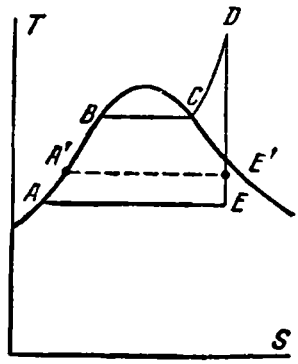


Fig. 13-19

It is important to note that the overall efficiency of the combined heat and power installation is less than that of cycle of the power installation. Fig. 13-19 shows this very clearly. This *Ts* diagram represents two cycles—the cycle of a condenser installation *ABCDE* and the cycle of a combined heat and power installation *A'BCDE'*; the initial parameters of the steam are identical in both cases. There is, of course, nothing unexpected in this. But the temperature and pressure of the steam when it leaves the turbine are higher in the heating cycle than in the condenser cycle: if this were not so it would not be possible to transmit heat to consumers because the temperature of the steam would be too low.

The economical working of heat and power stations cannot be judged by thermal efficiency alone or even by the real

efficiency of the station. The station supplies both electric power and heat to its customers so that there is a big economy in fuel.

What we have said above does not mean that an assessment of the quality of the cycle in a heat and power installation is not of interest, since it is important to know what part of the heat expended is converted into work and what part is used as useful heat. It is always advantageous to increase the amount of work obtained from the heat, bearing in mind that the energy value of heat is determined by the amount of work obtainable from it. It is, therefore, economically advantageous to supply heat to the consumer at the lowest permissible temperature.

This system of combined heat and power supply is being widely developed in the U.S.S.R. which occupies first place in the world both for the theoretical development of the system and its practical application.

13-7. The Intermediate Extraction of Steam. An installation employing counterpressure works rationally on the condition that the consumer uses all the waste steam from the turbines; thus, the use of steam by the power installation, i. e., the production of electric power, is determined by the amount of heat used by consumers—in other words, the whole installation works on a *compulsory* electrical and *free* heat time-tables. The condenser installation works on a free electric time-table because the passage of steam through the condenser, and, therefore, its capacity, is determined exclusively by the consumption of electricity. It is possible to produce electric power in the required quantities, irrespective of the consumption of low-pressure steam, by employing a turbine from which steam is extracted *at an intermediate pressure*. The schematic diagram of such an installation is given in Fig. 13-20: *A* is the boiler, *B*, the superheater,

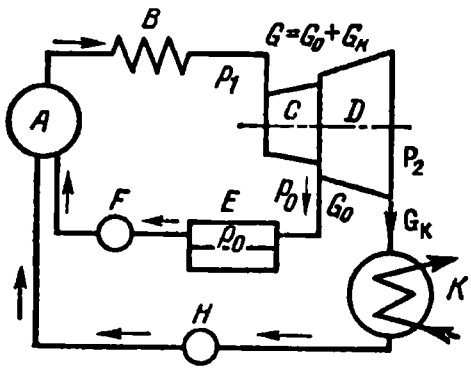


Fig. 13-20

C and D the turbine, consisting of two stages, the high-pressure stage C in which steam expands from pressure p_1 to pressure p_0 (that required by the heat consumer) and the low-pressure stage D, where the steam expands to pressure p_1 in the condenser K; E is the heat exchanger (the heat consumer); F and H are feed pumps. A quantity of steam with the weight G is injected into the turbine at pressure p_1; the amount of steam by weight required by the heat consumer, $G_0 < G$, is extracted from the turbine and branched off to the consumer E at pressure p_0. The remainder of the steam, $G_k = G - G_0$ continues to expand in the turbine to pressure p_2 and then goes to the condenser. The condensate from the condenser K and the heat-exchanger (in our case—the consumer) E is fed back into the boiler by the feed pumps F and H. In a turbine of this type, obviously a combination of a condenser turbine and a counterpressure turbine, the amount of steam, G_0, that goes to the heat consumer may change, when the turbine works at constant load, from zero to some maximum, and the production of electric power may vary if the consumption of heat is constant. If the consumption of heat increases while the generator load is constant, the amount of steam, G, supplied to the turbine, is increased by automatic regulation; since this immediately increases the capacity of the high-pressure stage of the turbine C, the regulator correspondingly reduces the amount of steam, G_k, passing to the low-pressure stage, D, thereby reducing its capacity; this results in an increase in the amount of steam, $G_0 = G - G_k$, which is extracted for the heat consumer. If the consumption of heat is constant ($G_0 = \text{const}$) and the power-station load is reduced, the regulator reduces the amount of steam, G, injected into the high-pressure stage of the turbine and also the part G_k that passes to the low-pressure stage so that the difference $G - G_k = G_0$ remains unchanged although the capacity is reduced. The theoretical maximum extraction of steam is in the case of the turbine working at full load and full counterpressure, when the entire steam that is injected into the turbine is used by the heat consumer, none of it passing to the condenser, i. e., $G_0 = G$ and $G_k = 0$. If no steam is extracted the turbine works as an ordinary condenser installation, i. e., $G = G_k$ and $G_0 = 0$.

Thus, it can be seen that turbines working with an intermediate extraction of steam must run on a sliding timetable for both heat and electricity which explains their

widespread use at *heat and power stations* since the peak consumption of electricity and heat rarely coincide.

From the standpoint of economy, the installation employing intermediate extraction of steam is naturally of lower efficiency than that employing counterpressure but approaches closer to it, the greater the amount of steam extracted, i. e., the less the amount of steam passed through condenser because the heat content of the steam passing into the condenser, from which the heat content of the condensate must be subtracted, is a pure loss and often a very big one (an average of 500 Cal/kg).

Summarising what has been said above on methods of ensuring the more economical use of steam power installations, we must come to the conclusion that the most effective means is that of combining the generation of electricity with the provision of heat for outside consumers; it is, in fact, the most highly-perfected method in modern energetics. In capitalist countries it is employed on a very small scale—in pre-revolutionary Russia it was completely unknown. Under socialist conditions combined heat and power supply is being very widely developed so that it may be regarded as a ruling principle in Soviet power engineering. The importance of combined power and heat supply was recognised by the Central Committee of the Communist Party of the Soviet Union as long ago as June 1931, when one of the directives of a plenary meeting held that month said, "The Central Committee considers that the further plan for the electrification of the country should include the all-round development of high-capacity heat and power stations..." This directive has been consistently followed by Soviet power engineers.

13-8. The Regenerative Cycle. The principle of the combined use of heat may be applied in ordinary condenser installations if the heat content of part of the live steam is used to heat the condensate; this makes the installation itself a heat consumer. The steam necessary to heat the condensate may be taken from any place in the turbine, according to the degree of heating required, so that the turbine will function with some of the steam extracted at an intermediate point.

A schematic diagram of such an installation is given in Fig. 13-21. G_k kg of condensate are mixed in the heater M

with G_0 kg of bled steam which, in turn, condensates at the pressure of extraction, p_0, raising the temperature of the remainder of the condensate to the temperature t_{s0} which corresponds to that pressure; this is the temperature at which the whole condensate, $G=G_0+G_k$ kg, is pumped into the boiler by the feed pump.

Since the turbine is designed exclusively for the generation of electricity and the heat of the steam extracted is not lost to the cycle, the thermal efficiency of the installation, η_t, determines, in the given case, not only the part of the expended

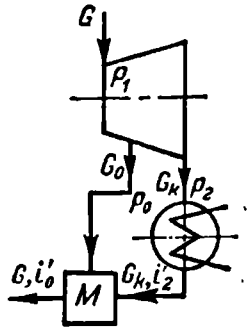


Fig. 13-21

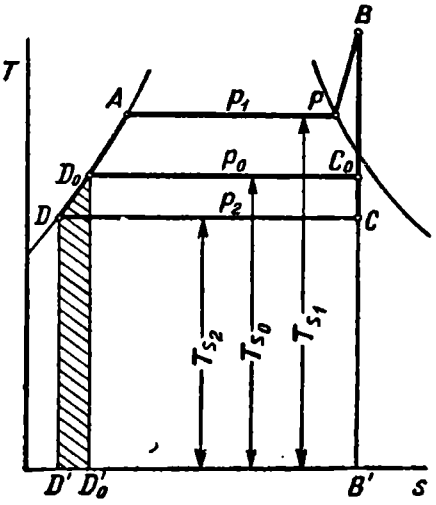


Fig. 13-22

heat that is converted into work, but also the economic use of heat in the entire installation.

In this case the steam performs two cycles: G_0 kg of steam bled from the turbine complete the cycle $APBC_0D_0$ (Fig. 13-22), and $G_k=G-G_0$ kg of steam passing into the condenser complete the cycle $APBCD$. The specific feature of the second cycle, in which it differs from the normal Rankine cycle, is the heating of the basic condensate from temperature t_{s2} to temperature t_{s1} in two stages: first, from t_{s2} to t_{s0} in the mixing heater M where it is heated by the bled steam (process DD_0) and then from t_{s0} to t_{s1} in the usual way in the boiler. The process C_0D_0 is that of the bled steam in the heater M.

We can obtain the total thermal efficiency of the installation, η_t, by the usual means of the relation of the work, Al, of 1 kg of steam to the amount of heat, q_1, consumed in

forming that steam. Actually heat is consumed only in the boiler, which receives the total condensate in the state indicated by point D_0, i. e., q_1=area $D_0APBB'D_0'$. The work, Al, is obtained in the following manner. If $g_0=\frac{G_0}{G}$, the relative amount of steam extracted, i. e., the amount of bled steam per kg of steam injected into the turbine, then this amount of steam, since it completes the cycle $APBC_0D_0$ will do an amount of work equal to g_0Al_1, where Al_1 is the work of 1 kg of steam indicated by the area $APBC_0D_0$, Al_1 being equal to $i_b-i_{c_0}$. The remaining amount of steam, $1-g_0$ kg, completes the cycle $APBCD$ and, therefore, does the work $(1-g_0)\,Al_2$, where Al_2 is the work of 1 kg of steam indicated by the area $APBCD$, Al_2 being equal to i_b-i_c. The total work of 1 kg of steam injected into the turbine is

$$Al=g_0Al_1+(1-g_0)\,Al_2$$

and the mean thermal efficiency is

$$\eta_t=\frac{Al}{q_1}=\frac{g_0Al_1+(1-g_0)\,Al_2}{q_1}=g_0\,\frac{Al_1}{q_1}+(1-g_0)\,\frac{Al_2}{q_1}. \quad (13\text{-}14)$$

By comparing the efficiency of this cycle with that of the normal Rankine cycle $APBCD$, without heating, we can explain the significance of the extraction of steam to heat the condenser (k), i. e.,

$$\eta_{t_{c_0}}=\frac{Al_2}{q_{1c_0}}=\frac{i_b-i_c}{i_b-i_2'},$$

where q_{1c_0} is indicated by area $DAPBB'D'$.

Substituting this value in equation 13-14, we get

$$Al_2=\eta_{t_{c_0}}q_{1c_0},$$

and also

$$\frac{Al_1}{q_1}=\eta_{t_0}=\frac{i_b-i_{c_0}}{i_b-i_0'}$$

where η_{t_0} is the thermal efficiency of the cycle $APBC_0D_0$ we get

$$\eta_t=g_0\eta_{t_0}+(1-g_0)\,\eta_{t_{c_0}}\frac{q_{1c_0}}{q_1}. \quad (13\text{-}15)$$

The shaded area in Fig. 13-22, $DD_0D_0'D'=q_{1c_0}-q_1$ gives us the amount of heat received by each kilogram of the basic condensate in the mixing heater from the bled steam that

condenses there, each kilogram of which gives up to the heater the amount of heat q_2 indicated by area $D_0C_0B'D_0'$. Since each kilogram of fresh steam is mixed with g_0 kg of bled steam and $1-g_0$ kg of basic condensate in the heater, we may write,

$$(1-g_0)(q_{1c_0}-q_1)=g_0q_2.$$

Replacing q_2 by an expression from the relation

$$\eta_{t_0}=1-\frac{q_2}{q_1},$$

that is,

$$q_2=(1-\eta_{t_0})q_1,$$

we get

$$(1-g_0)(q_{1c_0}-q_1)=g_0(1-\eta_{t_0})q_1 \qquad (13\text{-}16)$$

or

$$(1-g_0)\left(\frac{q_{1c_0}}{q_1}-1\right)=g_0(1-\eta_{t_0})$$

whence

$$\frac{q_{1c_0}}{q_1}=\frac{g_0}{1-g_0}(1-\eta_{t_0})+1.$$

Substituting this relation in equation 13-15, we get

$$\eta_t=g_0\eta_{t_0}+(1-g_0)\eta_{tc_0}\left[\frac{g_0}{1-g_0}(1-\eta_{t_0})+1\right]=$$
$$=g_0\eta_{t_0}+\eta_{tc_0}[g_0(1-\eta_{t_0})+1-g_0]=g_0\eta_{t_0}+\eta_{tc_0}(1-g_0\eta_{t_0})=$$
$$=g_0\eta_{t_0}+\eta_{tc_0}-g_0\eta_{t_0}\eta_{tc_0}=\eta_{tc_0}+g_0\eta_{t_0}(1-\eta_{tc_0}). \qquad (13\text{-}17)$$

We see from equation 13-17 that heating the condensate with steam bled from the turbine makes the installation thermally more economical because $\eta_t>\eta_{tc_0}$ and η_t itself increases as g_0 and η_{t_0}.

But the values of g_0 and η_{t_0}, other conditions being equal, are determined by the pressure of the steam extraction p_0, i. e., by the temperature, t_{s_0}, at which the condensate is heated. It is obvious that p_0 must determine η_{t_0}, and that it determines g_0 also can be seen from equation 13-16, the equation of the heat balance of the heater. If we write it thus

$$(1-g_0)(i_0'-i_2')=g_0(i_{c_0}-i_0'),$$

we get

$$g_0=\frac{i_0'-i_2'}{i_{c_0}-i_2'}, \qquad (13\text{-}18)$$

i. e., at the given p_1, t_1, and p_2 the pressure p_0 is sufficient to determine g_0.

A reduction of p_0 increases η_{t_0} but simultaneously decreases g_0, and vice versa, as can be established by some typical calculations. Under these circumstances it is obvious that there must be an optimum pressure for steam extraction and an optimum temperature at which the condensate is reheated (t_{s_0}) that will give the maximum η_t. This can be proved as follows.

The work, Al, of 1 kg of steam injected into the turbine, may be represented as the sum of the work Al_1 performed during expansion (before any steam is extracted) BC_0, and the work $(1-g_0)\,Al_2'$, performed by $1-g_0$ kg of steam remaining after the extraction and during its expansion C_0C, where Al_2' is the work of one kilogram of steam represented by the area D_0C_0CD. If we calculate the efficiency of this imaginary cycle D_0C_0CD

$$\eta_{t_2}=\frac{Al_2'}{q_1'}=\frac{i_{c_0}-i_c}{i_{c_0}-i_2'}$$

the total thermal efficiency of the installation may be expressed as follows:

$$\eta_t=\frac{Al}{q_1}=\frac{Al_1+(1-g_0)\,Al_2'}{q_1}=\frac{Al_1}{q_1}+(1-g_0)\,\frac{Al_2'}{q_1}=$$

$$=\eta_{t_0}+(1-g_0)\,\eta_{t_2}\frac{q_1'}{q_1}. \qquad (13\text{-}19)$$

From equation 13-18 we know that

$$1-g_0=1-\frac{i_0'-i_2'}{i_{c_0}-i_2'}=\frac{i_{c_0}-i_0'}{i_{c_0}-i_2'};$$

in addition to which

$$q_1'=i_{c_0}-i_2' \text{ and } q_1=i_b-i_0'.$$

Making the necessary substitutions, we may write equation 13-19 as

$$\eta_t=\eta_{t_0}+\eta_{t_2}\frac{i_{c_0}-i_0'}{i_{c_0}-i_2'}\times\frac{i_{c_0}-i_2'}{i_b-i_0'}=\eta_{t_0}+\eta_{t_2}\frac{i_{c_0}-i_0'}{i_b-i_0'}=$$

$$=\eta_{t_0}+\eta_{t_2}\frac{q_2}{q_1},$$

and since

$$\frac{q_2}{q_1}=1-\eta_{t_0},$$

$$\eta_t=\eta_{t_0}+\eta_{t_2}(1-\eta_{t_0}).$$

This last equation may be written as:

$$\eta_t = 1 - (1 - \eta_{t_0})(1 - \eta_{t_2}). \qquad (13\text{-}20)$$

Since any change in p_0 causes a change in η_{t_0} and η_{t_2} but in opposite directions, there obviously must be an optimum p_0 which can be found for each individual case by a number of experimental calculations.

As an example, let

$p_1 = 20$ ata, $t_1 = 350°$ C, $p_2 = 0.04$ ata, and $p_0 = 1$ ata;

from the *is* diagram and the tables we get:

$$i_b = 748.8 \text{ Cal/kg}; \; i_{c_0} = 604 \text{ Cal/kg}; \; i_c = 501 \text{ Cal/kg};$$
$$i'_0 = 99.19 \text{ Cal/kg}; \; i'_2 = 28.67 \text{ Cal/kg};$$

using these data we find that

$$\eta_{tc_0} = \frac{748.8 - 501}{748.8 - 28.67} = 0.344;$$
$$\eta_{t_0} = \frac{748.8 - 604}{748.8 - 99.19} = 0.224;$$
$$\eta_{t_2} = \frac{604 - 501}{604 - 28.67} = 0.179;$$
$$g_0 = \frac{99.19 - 28.67}{604 - 28.67} = 0.1225,$$

so that equation 13-17 becomes

$$\eta_t = 0.344 + 0.1225 \times 0.224 (1 - 0.344) = 0.362;$$

and the same figure is obtained from equation 13-20

$$\eta_t = 1 - (1 - 0.224)(1 - 0.179) = 0.363,$$

i. e., in this case the heating of the condensate by steam bled from the turbine at a pressure of 1 ata increases the theoretical use of the heat by

$$\frac{0.364 - 0.346}{0.346} \times 100 = 5.2\%.$$

By extracting steam from the turbine to heat the condensate we reduce the expenditure of fuel per kg of steam, on the one hand, but, on the other hand, reduce the work performed by each kilogram of steam injected into the turbine and, consequently, increase the specific expenditure of steam. Despite the contradictory nature of these two manifestations, the extraction of steam from the turbine always de-

creases the specific expenditure of heat, i. e., it increases the efficiency η_t, but the economy effected depends on the temperature of the extracted steam (i. e., on its pressure). Taking the figures of our example we may show that the pressure selected, $p_0=1$ ata, gives us $\eta_{t\max}$ at $p_0=18$ ata, $\eta_t=0.348$ and at $p_0=0.2$ ata, $\eta_t=0.357$.

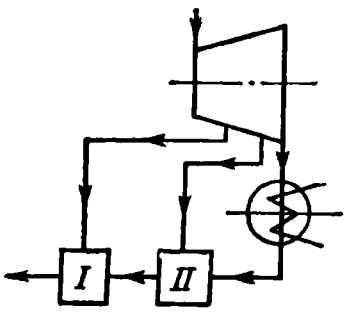


Fig. 13-23

Similarly it may be established that the greatest economy is effected when the steam is extracted from several places in different stages of the turbine and used in a series of heaters in the way shown schematically in Fig. 13-23 (two-stage heating). The greater the number of extractions, the higher the optimal heating temperature and the greater the economy, i. e., the greater thermal efficiency η_t of the installation.

Since the heat given up by the bled steam in the heaters is imparted to the condensate, this process is, to a certain extent, one of regeneration, since the heating of the feedwater is usually called a *regenerative* process. The economy effected is, on the average, the following:

at first extraction	4.5%
at two extractions	6.5%
at three extractions	7.5%
at four extractions	8%

i. e., the efficiency of each extraction is the less, the greater the number of extractions. In view of this and also of the greater cost of complicated installations, no more than three to five extractions are, as a rule, practiced.

Regenerative heating also provides better use of the heat in condenser installations in which steam is extracted at an intermediate stage for external heating purposes, the economy being the greater, the less the amount of steam extracted; as far as installations using counterpressure are concerned, the process does not afford any economy because the steam is used to the full without it; nevertheless, the use of regenerative heating provides a bigger output of electric power at the cost of the fuel expended on the reheater so that its use is always advisable because of the fuel economy.

Chapter Fourteen

REFRIGERATION CYCLES

14-1. Vapour Refrigerators. As we have seen, a refrigeration installation uses a cycle that is the opposite of that of a power installation; external work is expended on it and the working body takes heat from the bodies to be cooled at relatively low temperatures. Generally speaking, refrigerators may work on any gas or vapour; in modern practice the vapours used are mostly those of ammonia (NH_3), carbon dioxide (CO_2) and sulphur dioxide (SO_2), all of which are liquids with a low boiling point.

Fig. 14-1 is a schematic diagram of a vapour refrigerator that consists, in the main, of the compressor A, the condenser B, the throttle valve C and the refrigerator D. It functions in the following way: the piston of the compressor A, moving from left to right, sucks saturated ammonia vapour (or SO_2,

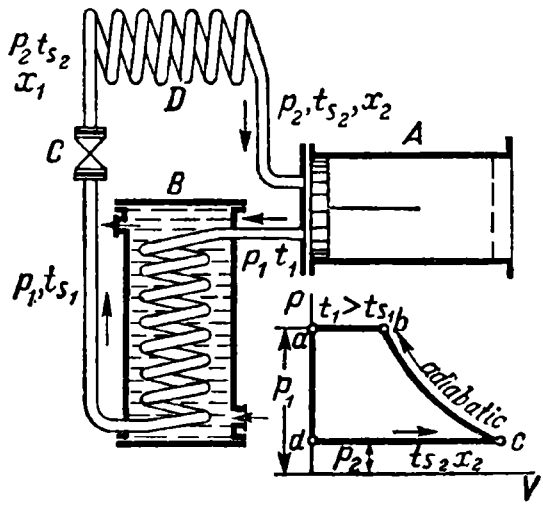


Fig. 14-1

CO_2) from the refrigerator with a quality, x_2, that is close to unity, at constant pressure p_2 and the corresponding temperature t_{s2}. The suction stroke is represented in the indicator diagram by the horizontal line *dc*. On the return stroke the vapour is compressed (theoretically) along the adiabatic *cb* to pressure p_1 and is superheated. At point *b* the force valve opens and the superheated vapour is pushed out of the cylinder by the piston at constant pressure p_1 into condenser *B* where it is cooled by running water and loses the heat both of superheating and evaporation, thus being converted into a liquid at pressure p_1 and the corresponding temperature t_{s1}. As it leaves the condenser the liquid ammonia passes through the throttle valve *C* where throttling reduces its pressure to p_2 and it is converted into a vapour-liquid mixture, whose quality is x_1 and whose temperature is t_{s2}. In the refrigerator the mixture receives heat from the medium to be cooled at constant pressure p_2 with the result that its quality improves from x_1 to x_2 at which it is again sucked in by the compressor piston.

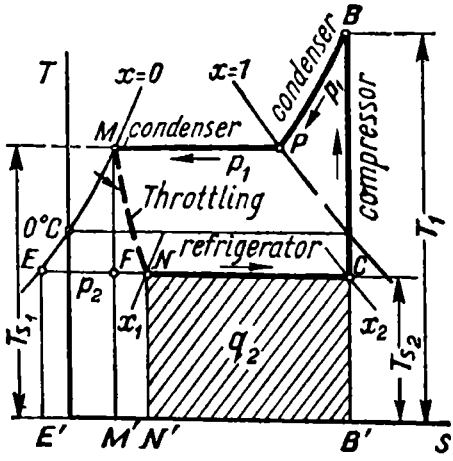


Fig. 14-2

14-2. The Heat Diagram of the Refrigeration Cycle. The cycle we have described is depicted in Fig. 14-2 as a *Ts* diagram: *CB* is the adiabatic compression in the compressor; *BPM* is the process in the condenser at p_1=const; *NC* is the process in the refrigerator at p_2 =const. The throttling process, typically irreversible, can only be shown in the diagram by a conventional line. This conventional curve is *MN*, the line of constant enthalpy (i=const) since the enthalpy does not change as a result of throttling (area $EMM'E'$=area $ENN'E'$, i being calculated from point *E*).

Along line *NC* the wet ammonia vapour receives the following amount of heat in the refrigerator

$$q_2 = \text{area } NCB'N' = i_c - i_N.$$

Heat is given up to the coolant only in the condenser in the quantity q_1 = area $MPBB'M'$; the work expended on one cycle, therefore, is

$$Al = q_1 - q_2 = \text{area } MPBB'M' - \text{area } NCB'N' =$$
$$= \text{area } MPBCNN'M'M = \text{area } MPBCE = i_b - i_c$$

(this is because area $EMM'E'$ = area $ENN'E'$ so that area EMF = area $FNN'M'$), i. e., the negative work of the cycle is equal to the available work of expansion BC; it is expended in driving the compressor in which the process CB takes place. Thus, we see that the graphic representation of the irreversible cycle is a purely conventional one; the work expended is not equal to the area of the cycle $MPBCN$, but is greater than that area.

14-3. Computation of the Refrigeration Cycle. The temperature t_{s1} and, therefore, the final pressure, p_1, of the compression stroke of the piston that corresponds to that temperature, is selected relevant to the temperature of the coolant used in the condenser and is usually a few degrees higher than the latter: for example, if the temperature of the water is 15°C we may assume that t_{s1} = 20°C. The temperature t_{s2} will be, on the average, —10°C. Pressures corresponding to this temperature are

	NH_3	CO_2	SO_2
p_1 =	8.74	58.15	3.35 ata
p_2 =	2.97	27	1.04 ata.

Since the enthalpy is identical at points M and N, we may write that

$$i'_2 + x_1 r_2 = i'_1,$$

where i'_1—the enthalpy of the liquid at pressure p_1;
i'_2—the enthalpy of the liquid at pressure p_2;
r'_2—the heat of steam formation at pressure p_2, so that

$$x_1 = \frac{i'_1 - i'_2}{r_2}. \qquad (14\text{-}1)$$

Equation 14-1 determines the quality (the degree of dryness) of the mixture at point where it enters the refrigerator (point N); its quality as it leaves the refrigerator (point C) is made to approximate unity, usually x_2 = 0.95. In this case the amount of heat taken from the medium being cooled

by each kilogram of the heat-carrier is

$$q_2 = (x_2 - x_1) r_2$$

and since

$$x_1 r_2 = i'_1 - i'_2 \text{ by equation 14-1,}$$

$$q_2 = x_2 r_2 - i'_1 + i'_2; \qquad (14\text{-}2)$$

this is known as the *cooling effect* of one kilogram of the heat-carrier for one cycle.

At $t_{s1} = 20°\,C$, $t_{s2} = -10°\,C$ and $x_2 = 0.95$, equation 14-1 gives us

NH_3	CO_2	SO_2	
$q_2 = 260$	38	79	Cal/kg.

The theoretical efficiency of the power cycle is assessed by its thermal efficiency,

$$\eta_t = \frac{Al}{q_1} = 1 - \frac{q_2}{q_1};$$

the greater the work, Al, and the less the waste heat, q_2, the higher the efficiency of the cycle. The main purpose of a refrigerating installation working on a reverse cycle is to obtain the greatest cooling effect, q_2, with the least expenditure of work, Al. The efficiency of the refrigerator is assessed by the relation

$$\varepsilon = \frac{q_2}{Al}, \qquad (14\text{-}3)$$

which is called the *refrigeration coefficient*. By substituting $Al = i_b - i_c$ and $q_2 = i_c - i_N$ we get

$$\varepsilon = \frac{i_c - i_N}{i_b - i_c}. \qquad (14\text{-}4)$$

Substituting the values of q_2 given above we get

NH_3	CO_2	SO_2
$\varepsilon = 7.6$	5.7	8.7.

Thus, we see that the most economical refrigerators are sulphur dioxide type; they are closely followed by ammonia installations.

Chapter Fifteen

DAMP AIR

15-1. The Basic Parameters of Damp Air. In a drying installation the heat-carrier is damp air. Damp air is a mixture of pure air and superheated or saturated steam. According to the Dalton law, the pressure of such a mixture is

$$p = p_a + p_{st},$$

p_a and p_{st} being the partial pressures of the air and the steam respectively. The highest possible pressure p_{st} at a given temperature is that of saturated steam, p_s, corresponding to the temperature of the mixture, i. e., the temperature of the moist air, t, as can be seen from the pv diagram in Fig. 15-1. In this case we have a mixture of air and saturated steam, the latter being either dry or wet. If the steam is dry, then its weight per cum of the mixture, i. e., its specific weight γ_{st} is equal to γ'', the specific weight of dry saturated steam at pressure p_s (or at temperature t); in such cases it is said that *the air is saturated with moisture*. If the steam is wet it is natural that the specific weight $\gamma_{st} > \gamma''$, i. e., *the air is oversaturated with moisture*; this case is rarely met with in engineering practice and is, therefore, of no interest to us. If, lastly, the weight of the steam in 1 cum of the mixture is $\gamma_{st} < \gamma''$, the steam is obviously superheated and *the air is not saturated*. Pressure p_{st} of the superheated steam at the given temperature, t, is, naturally, always lower than the pressure of saturation p_s as Fig. 15-1 clearly demonstrates.

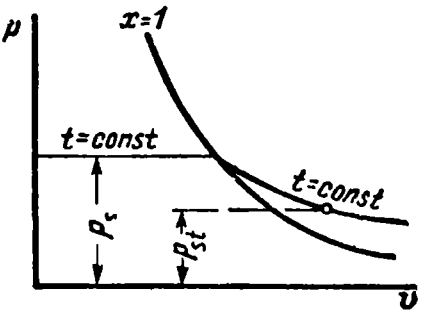


Fig. 15-1

The weight of the steam in 1 cum of damp air, i. e., *the specific weight of the steam in the mixture*, γ_{st}, *is known as the absolute moisture of the air.* The relation

$$\varphi = \frac{\gamma_{st}}{\gamma''}$$

is the *relative moisture*, or *degree of saturation*; this is the relation of the actual absolute moisture to the absolute moisture of saturated air at the given temperature.

In saturated air, the partial pressure p_s is fully determined by the temperature of the mixture, t, whose pressure can be anything greater than p_s, and, furthermore, the absolute moisture of the air, γ'', does not in any way depend on the pressure of the mixture, p, but only on the pressure p_s, that is, on the temperature of the air, t, so that 1 cum of damp air at 10 ata contains the same weight of steam as air at 1 ata and the same temperature, i. e.,

$$\gamma'' \frac{\text{kg}}{\text{cum}}.$$

If saturated damp air is cooled at constant pressure, γ'' will decrease with the temperature and the relative moisture φ will increase. When $\gamma_{st}=\gamma''$ we get $\varphi=1$, i. e., the air is saturated; further cooling leads to over-saturation and the moisture in it becomes drops of water, or dew. For this reason the temperature at which $\varphi=1$ is called the *condensation point* or *dew point*. It can be determined by using a hygrometer, or more precisely from the partial pressure of the steam, p_{st}, as the temperature of saturation at that pressure (from the tables for saturated steam); the pressure p_{st} is found by means of an instrument called a psychrometer.

The partial pressure of the steam in damp air is usually very low; for example, the pressure of the steam in saturated air, i. e., the maximum possible at the given temperature is

at $t=$	$-20°$	$0°$	$+20°$	$+40°$ C
$p_s=$	0.96	4.6	17.5	55 mm Hg.

In unsaturated air the partial pressure p_{st} is still lower; the gas laws, therefore, are fully applicable to superheated steam in damp air, in particular the equation

$$pv = RT.$$

For unsaturated steam a sufficiently close approximation will, therefore, be

$$p_{st}v_{st} = R_{st}T$$

and similarly for dry saturated steam at the same temperature

$$p_s v'' = R_{st}T,$$

i. e.,

$$p_{st}v_{st} = p_s v'',$$

or

$$\frac{p_{st}}{p_s} = \frac{v''}{v_{st}} = \frac{\gamma_{st}}{\gamma''} = \varphi. \qquad (15\text{-}1)$$

Therefore, having obtained the partial pressure of the steam, p_{st}, with a psychrometer, and the pressure of saturation, p_s, from the tables for the corresponding temperature of the air, t, we arrive at the relative moisture of the air, φ, as the relation $\frac{p_{st}}{p_s}$ and the absolute moisture as

$$\gamma_{st} = \varphi\gamma'',$$

taking γ'' from the tables for the given temperature t.

Since the partial pressure of the air is

$$p_a = p - p_{st}$$

its weight in 1 cum of the mixture, i. e., the specific weight γ_a, according to the equation of state, will be

$$\gamma_a = \frac{p_a}{R_a T} = \frac{p - p_{st}}{R_a T},$$

where $R_a = 29.27$, the gas constant of air;

p_a—the pressure in ksm.

The partial pressures p_a and p_{st} are usually measured in millimetres Hg; applying equation 15-1 we get the value of p_a as

$$\gamma_a = \frac{10{,}333p_a}{760 \times 29.27T} = 0.465\,\frac{p - \varphi p_s}{T}$$

so that the specific weight of the damp air is

$$\gamma = \gamma_a + \gamma_{st} = 0.465\,\frac{p - \varphi p_s}{T} + \varphi\gamma''. \qquad (15\text{-}2)$$

The composition of damp air may be determined by the content, by volume, of air r_a, and steam r_{st} which, by

equation 1-41 are

$$r_a = \frac{p_a}{p} \text{ and } r_{st} = \frac{p_{st}}{p} \text{ respectively.}$$

In this case the gas constant of damp air by equation 1-40 will be

$$R = \frac{848}{\mu_a r_a + \mu_{st} r_{st}} = \frac{848}{28.95 \frac{p_a}{p} + 18.016 \frac{p_{st}}{p}} =$$

$$= \frac{848}{28.95 \frac{p - p_{st}}{p} + 18.016 \frac{p_{st}}{p}} = \frac{848}{28.95 - 10.93 \frac{p_{st}}{p}} =$$

$$= \frac{848}{28.95 - 10.93\varphi \frac{p_s}{p}}, \quad (15\text{-}3)$$

and the mean molecular weight is

$$\mu = \frac{848}{R} = 28.95 - 10.93\varphi \frac{p_s}{p}, \quad (15\text{-}4)$$

i. e., damp air is always lighter than dry air at the same pressure and temperature.

In drying installations the composition of damp air is determined by the *moisture content* which is the ratio of steam to pure air in the mixture, or, which is the same thing, the ratio of steam to air content by weight:

$$d = \frac{G_{st}}{G_a} = \frac{g_{st}}{g_a}.$$

By equation 1-36

$$g_{st} = \frac{\mu_{st}}{\mu} r_{st} \text{ and } g_a = \frac{\mu_a}{\mu} r_a,$$

so that

$$d = \frac{g_{st}}{g_a} = \frac{\mu_{st}}{\mu_a} \times \frac{r_{st}}{r_a} = \frac{18.016}{28.95} \times \frac{p_{st}}{p_a} = 0.622 \frac{p_{st}}{p - p_{st}}. \quad (15\text{-}5)$$

Changes in the state of damp air do not usually bring about a change in the weight of the air content, but the steam content (by weight) may be reduced by condensation (rarely) or increased as a result of evaporation from the material being dried (the most frequent case). It is, therefore, advisable to base all calculations on 1 kg of dry air; the moisture, therefore, is calculated on the basis of 1 kg of dry air. In particular, the enthalpy of damp air refers to

1 kg of dry air, i. e., to $(1+d)$ kg of humid air. This enthalpy is, therefore, the total enthalpy, I, which is the sum of the enthalpy i_a of 1 kg of dry air and the enthalpy of d kg of steam, i. e.,

$$I = i_a + di_{st},$$

where i_{st} is the enthalpy of 1 kg of dry air. If the enthalpy is calculated, as is usually done, from 0° C and if it is assumed that $c_p = 0.24$ Cal/kg × deg for dry air, then

$$i_a = 0.24t.$$

As far as i_{st} is concerned this relation is accurate enough:

$$i_{st} = 595 + 0.46t$$

in which case

$$I = 0.24t + d(595 + 0.46t). \qquad (15\text{-}6)$$

The enthalpy I plays an important role in calculations because in practical work the engineer has to deal with changes in damp air at constant pressure, i. e., at normal atmospheric pressure.

When damp air that is not oversaturated is heated at constant pressure the composition of the mixture does not change, nor does the gas constant R of the mixture change; the partial pressures p_{st} and p_a, therefore, also remain unchanged; the absolute moisture γ_{st} naturally does not change, nor does the moisture content d. The relative moisture (degree of saturation), φ, does, however, change, because p_s increases as the temperature rises so that, by equation 15-1, φ decreases. By cooling damp air it is possible to bring it down to the dew point.

15-2. The *Id* Diagram for Damp Air. For the solution of practical problems arising out of the drying of damp or wet materials with the aid of dry or slightly damp air it is necessary to know how much steam can be absorbed by 1 kg of pure air at the given temperature before the saturation point is reached. These and similar calculations are best made graphically with the aid of diagrams and nomograms. The most widespread of the many graphical methods proposed by various authors is that of Professor L. K. Ramsin, proposed in 1918, which uses an *Id* diagram—the abscissa being the moisture content d, and the ordinates the enthalpy of the damp air I (for 1 kg of dry air). For the sake of con-

venience the axes are set at an angle of 135°; since part of the diagram below the horizontal axis and passing through the point of origin of the coordinates is of no practical interest, the divisions of the axis of the abscissa are transferred to the horizontal axis vertically, and the moisture is calculated from this axis.

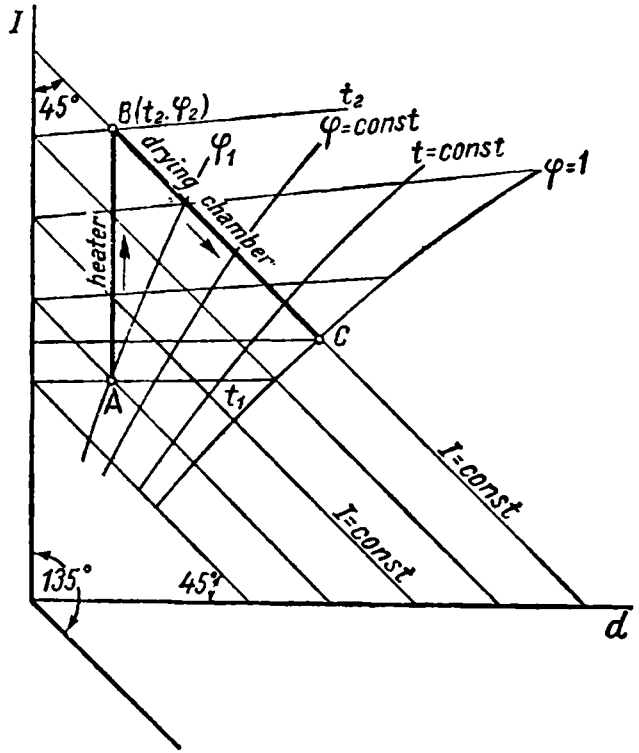


Fig. 15-2

On the graph we plot a network of lines I=const which are straight lines at an angle of 45° to the axes, and a network of isotherms which will also be straight lines (by equation 15-6) when the steam is superheated, and will have the equation

$$I = a + bd$$

where a and b have their own value for each value of t (Fig. 15-2).*

* In cases when the steam is wet, i. e., in the area of the Id diagram to the right of the curve $\varphi=1$, the isotherms are almost identical with the straight lines I=const (actually they are slightly closer to the horizontal).—*Ed.*

We then find on each isotherm a point with an identical value of φ; for this purpose, the corresponding

$$p_{st} = \varphi p_s$$

is determined from equation 15-1 and the corresponding value of d from equation 15-5.

Points at which φ is identical give the curve φ=const. Curve φ=1 is a sort of *threshold curve*, the curve of saturation.

The diagram is constructed for a definite barometric pressure, p, for example p=745 mm Hg, but will be accurate enough if there are small deviations from that pressure.

The process taking place in the drying chamber may be divided into two processes: at first air with a relative moisture of φ_1 at a temperature of t_1 (point A in the diagram) passes through the *heater* where its temperature is raised to t_2 and its relative moisture is reduced to φ_2. This process takes place at d=const and, therefore, corresponds to the vertical line AB in the diagram. The differences in the ordinates, $I_B - I_A$, gives us the heat consumed by the heater to heat 1 kg of dry air. The hot air then passes to the drying chamber where the material being dried loses its moisture through evaporation under the action of the hot air and the air itself becomes moist. This drying process takes place at I=const, because, although part of the enthalpy of the air is expended on the evaporation of moisture, it is returned to the mixture as the enthalpy of the steam obtained. Thus, the process in the drying chamber is represented by the section BC of the line I_B=const. Point C is the dew point; it is obviously not advisable to continue the process beyond point C because the steam would condense and moisture would be returned to the material being dried. The difference $d_C - d_A$ gives the amount of moisture evaporated in the drying chamber per kg of dry air.

Appendices

Appendix I

Mean Molar Heat Capacity of Gases at Constant Pressure from Spectroscopic Data (Cal per Mol/deg)

°C	O_2	N_2	H_2	CO	CO_2	H_2O	Air
0	6.993	6.975	6.841	6.958	8.614	7.978	6.960
100	7.058	6.978	6.909	6.972	9.142	8.034	6.962
200	7.152	6.996	6.946	7.005	9.610	8.118	6.996
300	7.265	7.030	6.963	7.056	9.997	8.224	7.051
400	7.380	7.081	6.976	7.121	10.332	8.342	7.117
500	7.491	7.143	6.989	7.196	10.650	8.469	7.190
600	7.593	7.212	7.007	7.274	10.945	8.602	7.266
700	7.686	7.283	7.029	7.353	11.205	8.740	7.342
800	7.771	7.354	7.055	7.430	11.438	8.881	7.415
900	7.843	7.423	7.086	7.503	11.774	9.023	7.486
1000	7.916	7.490	7.120	7.572	11.837	9.166	7.553
1100	7.979	7.554	7.158	7.637	12.010	9.307	7.616
1200	8.036	7.614	7.198	7.698	12.165	9.445	7.675
1300	8.090	7.670	7.240	7.755	12.310	9.581	7.731
1400	8.142	7.724	7.283	7.808	12.442	9.711	7.784
1500	8.191	7.774	7.326	7.857	12.564	9.838	7.833
1600	8.237	7.821	7.370	7.904	12.677	9.961	7.879
1700	8.281	7.865	7.414	7.947	12.780	10.079	7.923
1800	8.323	7.906	7.458	7.987	12.877	10.193	7.965
1900	8.364	7.945	7.501	8.025	12.967	10.300	8.004
2000	8.404	7.982	7.544	8.061	13.051	10.404	8.041
2100	8.443	8.017	7.585	8.094	13.130	10.503	8.076
2200	8.480	8.050	7.626	8.126	13.203	10.599	8.110
2300	8.517	8.081	7.666	8.156	13.273	10.691	8.142
2400	8.552	8.110	7.705	8.184	13.340	10.779	8.172
2500	8.587	8.139	7.754	8.211	13.402	10.863	8.202
2600	8.620	8.165	7.780	8.236	13.461	10.943	8.230
2700	8.652	8.191	7.817	8.260	13.516	11.021	8.256
2800	8.684	8.215	7.852	8.283	13.573	—	8.282
2900	8.714	8.238	7.886	8.305	13.624	—	8.306
3000	8.745	8.260	7.920	8.326	13.670	—	8.330
μ	32	28.016	2.0154	28.0	44.0	18.015	28.96
μv	22.4	22.402	22.41	22.393	22.26	22.41	22.4

True Molar Heat Capacity of Gases at Constant Pressure from Spectroscopic Data (Cal per Mol/deg)

°C	O_2	N_2	H_2	CO	CO_2	H_2O	Air
0	6.993	6.975	6.841	6.958	8.614	7.978	6.960
100	7.138	6.989	6.962	6.996	9.640	8.104	6.980
200	7.370	7.045	6.991	7.088	10.482	8.313	7.094
300	7.610	7.160	7.003	7.232	11.059	8.564	7.234
400	7.836	7.313	7.027	7.408	11.607	8.835	7.401
500	8.024	7.472	7.065	7.582	12.204	9.120	7.564
600	8.179	7.635	7.123	7.750	12.605	9.410	7.724
700	8.308	7.783	7.198	7.899	12.925	9.718	7.867
800	8.411	7.916	7.284	8.029	13.204	10.018	7.992
900	8.499	8.036	7.380	8.143	13.44	10.306	8.104
1000	8.574	8.143	7.485	8.244	13.64	10.585	8.204
1100	8.638	8.236	7.589	8.331	13.82	10.847	8.290
1200	8.690	8.315	7.691	8.405	13.96	11.091	8.362
1300	8.785	8.383	7.791	8.468	14.10	11.31	8.435
1400	8.844	8.446	7.889	8.524	14.22	11.52	8.497
1500	8.901	8.501	7.984	8.575	14.32	11.71	8.552
1600	8.958	8.551	8.074	8.620	14.40	11.89	8.602
1700	9.013	8.594	8.159	8.658	14.48	12.05	8.648
1800	9.073	8.630	8.239	8.690	14.55	12.18	8.687
1900	9.133	8.664	8.315	8.721	14.62	12.30	8.728
2000	9.190	8.696	8.386	8.749	14.68	12.43	8.765
2100	9.244	8.726	8.453	8.776	14.74	12.55	8.799
2200	9.296	8.754	8.515	8.801	14.79	12.67	8.832
2300	9.344	8.779	8.574	8.824	14.83	12.76	8.862
2400	9.400	8.802	8.630	8.844	14.87	12.84	8.889
2500	9.434	8.824	8.684	8.864	14.91	12.92	8.916
2600	9.474	8.842	8.735	8.881	14.95	13.00	8.938
2700	9.512	8.859	8.783	8.896	14.99	13.08	8.959
2800	9.553	8.875	8.829	8.910	15.03	—	8.990
2900	9.594	8.890	8.873	8.924	15.07	—	9.001
3000	9.634	8.904	8.912	8.936	15.11	—	9.020
μ	32	28.016	2.0154	28.0	44.0	18.015	28.96
μv	22.4	22.402	22.41	22.393	22.26	22.41	22.4

Mean Weight Heat Capacity of Gases per Unit at Constant Pressure from Spectroscopic Data (Cal per kg/deg)

°C	O_2	N_2	H_2	CO	CO_2	H_2O	Air
0	0.219	0.243	3.394	0.249	0.196	0.443	0.240
100	0.221	0.249	3.428	0.249	0.208	0.446	0.240
200	0.224	0.250	3.447	0.250	0.218	0.451	0.242
300	0.227	0.251	3.455	0.252	0.227	0.457	0.243
400	0.231	0.253	3.461	0.254	0.235	0.463	0.246
500	0.234	0.255	3.468	0.257	0.242	0.470	0.248
600	0.237	0.257	3.477	0.260	0.249	0.478	0.251
700	0.240	0.260	3.488	0.263	0.255	0.485	0.254
800	0.243	0.263	3.501	0.265	0.260	0.493	0.256
900	0.245	0.265	3.516	0.268	0.265	0.501	0.259
1000	0.247	0.267	3.533	0.270	0.269	0.509	0.261
1100	0.249	0.270	3.552	0.273	0.273	0.517	0.263
1200	0.251	0.272	3.572	0.275	0.277	0.524	0.265
1300	0.253	0.274	3.592	0.277	0.280	0.532	0.267
1400	0.254	0.276	3.614	0.279	0.283	0.539	0.269
1500	0.256	0.278	3.635	0.281	0.286	0.546	0.270
1600	0.257	0.279	3.657	0.282	0.288	0.553	0.272
1700	0.259	0.281	3.679	0.284	0.291	0.560	0.274
1800	0.260	0.282	3.701	0.285	0.293	0.566	0.275
1900	0.261	0.284	3.722	0.287	0.295	0.572	0.276
2000	0.263	0.285	3.743	0.288	0.297	0.578	0.278
2100	0.264	0.286	3.764	0.289	0.298	0.583	0.279
2200	0.265	0.287	3.784	0.290	0.300	0.588	0.280
2300	0.266	0.288	3.804	0.291	0.302	0.593	0.281
2400	0.267	0.290	3.823	0.292	0.303	0.598	0.282
2500	0.268	0.291	3.847	0.293	0.305	0.603	0.283
2600	0.269	0.291	3.860	0.294	0.306	0.607	0.284
2700	0.270	0.292	3.879	0.295	0.307	0.611	0.285
2800	0.271	0.293	3.896	0.296	0.309	—	0.286
2900	0.272	0.294	3.913	0.297	0.310	—	0.287
3000	0.273	0.295	3.930	0.297	0.311	—	0.288

p, kg-sq cm \ t° C	180	200	220	240	260	280	300	320	340	360	380	400	420
1	0.475	0.474	0.473	0.473	0.474	0.475	0.475	0.476	0.476	0.477	0.478	0 479	0.481
5	0.533	0.520	0 514	0.511	0.509	0.508	0.507	0.506	0.504	0.504	0.504	0 503	0.503
10	—	0.577	0.566	0.556	0.548	0.544	0.540	0.536	0.533	0.530	0.528	0 527	0.525
20	—	—	0.681	0.653	0.626	0.613	0.603	0.594	0 586	0.579	0.573	0.568	0.564
30	—	—	—	0.746	0.709	0.687	0.669	0.653	0.640	0.629	0.620	0 612	0.605
40	—	—	—	—	0.832	0.779	0.749	0.723	0.700	0.681	0.667	0 655	0.645
50	—	—	—	—	—	0.879	0.828	0.788	0.761	0.738	0.717	0.700	0.686
60	—	—	—	—	—	0.981	0.919	0.873	0.833	0.799	0.771	0.747	0.728
70	—	—	—	—	—	—	1 039	0.972	0.915	0.866	0 829	0.796	0.773
80	—	—	—	—	—	—	1 207	1.090	1 008	0.943	0.893	0.855	0.824
90	—	—	—	—	—	—	—	1.217	1 113	1.027	0.964	0 915	0.876
100	—	—	—	—	—	—	—	1.366	1.236	1.127	1.044	0.982	0.934
110	—	—	—	—	—	—	—	1.550	1.384	1.235	1.136	1.059	0.999
120	—	—	—	—	—	—	—	—	1.585	1 360	1.235	1.140	1.068
130	—	—	—	—	—	—	—	—	1.869	1.521	1.355	1.236	1.147
140	—	—	—	—	—	—	—	—	2.261	1.718	1.492	1.336	1.232
150	—	—	—	—	—	—	—	—	—	1.975	1.654	1.462	1.330
160	—	—	—	—	—	—	—	—	—	2.307	1.850	1.604	1.440
170	—	—	—	—	—	—	—	—	—	2.816	2.113	1.777	1.571
180	—	—	—	—	—	—	—	—	—	—	2.462	1.991	1.729
190	—	—	—	—	—	—	—	—	—	—	2.965	2.264	1.905
200	—	—	—	—	—	—	—	—	—	—	3.704	2.629	2.161
210	—	—	—	—	—	—	—	—	—	—	—	3.176	2.502
220	—	—	—	—	—	—	—	—	—	—	—	4.111	3.058

Steam Computed from the Temperature (Cal per kg/deg)

440	460	480	500	520	540	560	580	600	620	640	660	680	700
0.482	0.483	0.484	0.485	0.487	0.488	0.489	0.491	0.492	0.493	0.495	0.496	0.498	0.499
0.504	0.504	0 504	0.505	0.505	0.506	0.507	0.508	0.508	0.510	0.511	0.512	0.513	0.514
0.524	0.524	0.523	0.523	0.523	0.523	0.523	0.523	0.524	0.524	0.525	0.525	0.526	0.527
0.561	0.559	0.557	0.555	0.553	0.552	0.551	0.550	0.549	0.549	0.548	0.548	0.548	0.548
0.599	0.594	0.589	0.586	0.583	0.580	0.577	0.575	0.573	0.572	0.571	0.570	0.569	0.568
0.636	0.629	0 622	0.616	0.611	0.607	0.603	0.600	0.597	0.594	0.592	0.590	0.589	0.587
0.673	0.663	0.654	0 646	0.640	0.634	0.629	0.624	0.620	0.616	0.613	0.610	0.608	0.606
0.712	0.699	0.687	0.677	0.669	0.661	0.654	0.648	0.643	0.638	0.634	0.630	0.627	0.624
0.754	0.737	0.722	0.710	0.699	0.690	0.681	0.673	0.667	0.661	0.656	0.651	0.647	0.643
0.798	0.777	0.760	0.744	0.731	0.719	0.708	0.699	0.691	0.684	0.678	0.672	0.667	0.662
0.845	0.820	0.798	0.779	0.763	0.749	0.737	0.726	0.716	0.708	0.700	0.693	0.687	0.682
0.896	0 865	0.839	0.817	0.798	0.781	0.766	0.754	0.743	0.733	0.724	0.716	0.708	0.702
0.952	0.915	0.884	0.857	0.835	0.816	0.799	0.784	0.771	0.759	0.748	0.739	0.731	0.723
1.012	0.967	0.930	0.899	0.873	0.851	0.831	0.814	0.799	0.785	0.773	0.763	0.753	0.745
1.079	1.025	0.981	0.946	0.915	0.889	0.866	0.847	0.829	0.814	0.800	0.788	0.777	0.767
1.151	1.086	1.035	0.994	0.959	0.929	0.903	0 881	0.861	0.843	0.828	0.815	0.802	0.791
1.232	1.155	1.095	1.047	1 007	0.972	0.943	0.918	0.895	0.875	0.858	0.842	0.828	0.816
1.322	1.232	1.162	1.106	1.059	1.019	0.986	0.957	0.932	0.910	0.890	0.873	0.857	0.843
1.427	1.319	1.237	1.171	1.118	1.072	1.034	1.001	0.972	0.947	0.925	0.905	0.888	0.872
1.551	1.421	1.323	1.247	1.184	1.132	1.088	1.050	1.018	0.990	0.965	0.943	0.923	0.905
1.699	1.541	1.424	1.333	1.260	1.200	1.149	1.106	1 069	1.037	1.009	0.984	0.962	0.942
1.880	1.687	1.546	1.437	1.350	1.280	1.221	1.172	1.129	1.093	1.062	1.034	1.008	0.984
2.129	1.882	1.707	1.573	1.470	1.385	1.315	1.257	1.207	1.164	1.127	1.094	1.065	1.038
2.521	2.183	1.951	1.780	1.648	1.542	1.455	1.383	1.322	1.270	1.225	1.185	1.150	1.118

The figures to the left of the black line refe

p, kg per sqcm		40°	60°	80°	100°	120°	140°	160°
0.05	v	29.42	31.31	33.19	35.08	36.96	38.85	40.73
	t	614.8	623.9	633.0	642.1	651.1	660.2	669.4
	s	2.0164	2.0439	2.0703	2.0953	2.1190	2.1415	2.163
0.06	v	24.50	26.08	27.65	29.23	30.80	32.37	33.94
	t	614.8	623.9	632.9	642.1	651.1	660.2	669.4
	s	1.9965	2.0237	2.0500	2.0751	2.0988	2.1214	2.143
0.08	v	1.0079	19.56	20.74	21.92	23.10	24.28	25.46
	t	40.0	623.8	632.9	642.1	651.1	660.1	669.3
	s	0.1365	1.9919	2.0183	2.0432	2.0669	2.0896	2.111
0.10	v	1.0079	15.64	16.58	17.53	18.47	19.42	20.36
	t	40.0	623.7	632.8	642.0	651.0	660.1	669.3
	s	0.1365	1.9672	1.9935	2.0186	2.0423	2.0649	2.086
0.12	v	1.0079	13.02	13.81	14.60	15.39	16.18	16.96
	t	40.0	623.6	632.8	641.9	651.0	660.1	669.3
	s	0.1365	1.9470	1.9733	1.9984	2.0221	2.0448	2.066
0.16	v	1.0079	9.759	10.36	10.95	11.54	12.13	12.72
	t	40.0	623.4	632.6	641.8	650.9	660.0	669.2
	s	0.1365	1.9150	1.9415	1.9666	1.9903	2.0129	2.034
0.20	v	1.0079	7.797	8.277	8.752	9.226	9.699	10.17
	t	40.0	623.2	632.5	641.7	650.8	659.9	669.1
	s	0.1365	1.8903	1.9166	1.9417	1.9655	1.9882	2.009
0.24	v	1.0079	1.0171	6.893	7.290	7.685	8.080	8.474
	t	40.0	60.0	632.3	641.5	650.7	659.9	669.1
	s	0.1365	0.1984	1.8962	1.9215	1.9454	1.9681	1.989
0.30	v	1.0079	1.0171	5.507	5.826	6.143	6.459	6.776
	t	40.0	60.0	632.1	641.4	650.6	659.8	669.0
	s	0.1365	0.1984	1.8713	1.8965	1.9204	1.9431	1.964
0.40	v	1.0079	1.0171	4.123	4.365	4.604	4.842	5.079
	t	40.0	60.0	631.7	641.1	650.3	659.5	668.8
	s	0.1365	0.1984	1.8389	1.8646	1.8887	1.9116	1.933
0.50	v	1.0079	1.0171	1.0290	3.487	3.679	3.870	4.060
	t	40.0	60.0	80.0	640.8	650.1	659.3	668.6
	s	0.1365	0.1984	0.2567	1.8397	1.8639	1.8866	1.908
0.60	v	1.0079	1.0171	1.0290	2.902	3.063	3.223	3.382
	t	40.0	60.0	80.0	640.4	649.9	659.2	668.5
	s	0.1365	0.1984	0.2567	1.8186	1.8432	1.8662	1.888
0.70	v	1.0079	1.0171	1.0290	2.484	2.623	2.760	2.896
	t	40.0	60.0	80.0	640.2	649.7	659.0	668.3
	s	0.1365	0.1984	0.2567	1.8012	1.8257	1.8488	1.870

SUPERHEATED STEAM

to water for which v is expressed in cudm per kg

180°	200°	220°	240°	260°	280°	300°	t / p, kg per sqcm	
42.62	44.50	46.39	48.27	50.15	52.04	53.92	v	0.05
678.6	687.8	697.0	706.4	715.8	725.2	734.8	i	
2.1839	2.2039	2.2231	2.2415	2.2595	2.2769	2.2938	s	
35.51	37.08	38.65	40.22	41.79	43.36	44.93	v	0.06
678.5	687.8	697.0	706.4	715.8	725.2	734.8	i	
2.1638	2.1838	2.2030	2.2214	2.2393	2.2568	2.2737	s	
26.64	27.82	28.99	30.17	31.35	32.52	33.70	v	0.08
678.5	687.8	697.0	706.3	715.7	725.2	734.8	i	
2.1319	2.1518	2.1711	2.1897	2.2076	2.2249	2.2418	s	
21.30	22.24	23.19	24.13	25.07	26.02	26.96	v	0.10
678.5	687.7	697.0	706.3	715.7	725.2	734.8	i	
2.1073	2.1273	2.1465	2.1650	2.1830	2.2003	2.2172	s	
17.75	18.54	19.32	20.11	20.89	21.68	22.46	v	0.12
678.5	687.7	697.0	706.3	715.7	725.2	734.8	i	
2.0872	2.1072	2.1264	2.1450	2.1630	2.1803	2.1972	s	
13.31	13.90	14.49	15.08	15.66	16.25	16.84	v	0.16
678.4	687.7	696.9	706.2	715.7	725.2	734.8	i	
2.0554	2.0753	2.0946	2.1132	2.1310	2.1484	2.1654	s	
10.65	11.12	11.59	12.06	12.54	13.01	13.48	v	0.20
678.3	687.6	696.9	706.2	715.6	725.2	734.8	i	
2.0306	2.0506	2.0698	2.0885	2.1065	2.1238	2.1409	s	
8.869	9.262	9.656	10.05	10.45	10.84	11.23	v	0.24
678.3	687.6	696.9	706.2	715.6	725.1	734.7	i	
2.0105	2.0305	2.0497	2.0683	2.0863	2.1037	2.1206	s	
7.092	7.407	7.722	8.038	8.352	8.667	8.983	v	0.30
678.2	687.5	696.8	706.1	715.5	725.1	734.7	i	
1.9856	2.0058	2.0250	2.0436	2.0616	2.0790	2.0959	s	
5.317	5.553	5.790	6.026	6.263	6.500	6.736	v	0.40
678.0	687.4	696.7	706.1	715.5	725.1	734.7	i	
1.9542	1.9742	1.9934	2.0120	2.0300	2.0475	2.0644	s	
4.250	4.440	4.629	4.819	5.008	5.197	5.387	v	0.50
677.9	687.2	696.6	705.9	715.4	725.0	734.6	i	
1.9294	1.9494	1.9686	1.9873	2.0053	2.0228	2.0397	s	
3.540	3.700	3.858	4.016	4.174	4.331	4.489	v	0.60
677.7	687.1	696.5	705.9	715.3	724.9	734.5	i	
1.9089	1.9289	1.9483	1.9669	1.9849	2.0023	2.0193	s	
3.033	3.169	3.304	3.440	3.576	3.711	3.847	v	0.70
677.5	687.0	696.4	705.8	715.3	724.9	734.5	i	
1.8916	1.9118	1.9311	1.9499	1.9679	1.9853	2.0024	s	

p, kg per sq cm		t 40°	60°	80°	100°	120°	140°	160°
0.80	v	1.0079	1.0171	1.0289	2.169	2.292	2.413	2.532
	i	40.0	60.0	80.0	639.9	649.4	658.8	668.3
	s	0.1365	0.1984	0.2567	1.7859	1.8107	1.8339	1.8554
0.90	v	1.0079	1.0171	1.0289	1.925	2.035	2.143	2.249
	i	40.0	60.0	80.0	639.5	649.2	658.6	668.0
	s	0.1365	0.1984	0.2567	1.7722	1.7973	1.8206	1.842
1.0	v	1.0079	1.0170	1.0289	1.730	1.830	1.926	2.023
	i	40.0	60.0	80.0	639.2	649.0	658.4	667.8
	s	0.1365	0.1984	0.2567	1.7603	1.7851	1.8083	1.830
1.2	v	1.0078	1.0170	1.0289	1.0435	1.521	1.602	1.683
	i	40.0	60.0	80.0	100.1	648.5	658.0	667.5
	s	0.1365	0.1984	0.2567	0.3121	1.7640	1.7875	1.809
1.4	v	1.0078	1.0170	1.0289	1.0435	1.300	1.371	1.440
	i	40.0	60.0	80.0	100.1	648.0	657.7	667.2
	s	0.1365	0.1984	0.2567	0.3121	1.7461	1.7700	1.792
1.6	v	1.0078	1.0170	1.0289	1.0435	1.135	1.197	1.258
	i	40.0	60.0	80.0	100.1	647.5	657.3	666.9
	s	0.1365	0.1984	0.2567	0.3121	1.7306	1.7548	1.777
1.8	v	1.0078	1.0170	1.0289	1.0435	1.006	1.062	1.117
	i	40.0	60.0	80.0	100.1	647.0	656.9	666.6
	s	0.1365	0.1984	0.2567	0.3121	1.7166	1.7409	1.763
2.0	v	1.0078	1.0170	1.0289	1.0435	0.9027	0.9545	1.003
	i	40.0	60.0	80.0	100.1	646.5	656.5	666.4
	s	0.1365	0.1984	0.2567	0.3121	1.7043	1.7284	1.751
2.5	v	1.0078	1.0170	1.0289	1.0434	1.0603	0.7597	0.800
	i	40.0	60.0	80.0	100.1	120.3	655.6	665.5
	s	0.1365	0.1984	0.2567	0.3121	0.3647	1.7024	1.725
3.0	v	1.0078	1.0170	1.0288	1.0434	1.0602	0.6296	0.664
	i	40.0	60.0	80.0	100.1	120.3	654.5	664.7
	s	0.1365	0.1983	0.2567	0.3121	0.3647	1.6802	1.704
4.0	v	1.0077	1.0169	1.0288	1.0433	1.0602	1.0798	0.494
	i	40.1	60.0	80.0	100.1	120.3	140.7	663.1
	s	0.1365	0.1983	0.2566	0.3120	0.3646	0.4150	1.669
5.0	v	1.0077	1.0168	1.0287	1.0433	1.0601	1.0797	0.391
	i	40.1	60.0	80.0	100.1	120.3	140.7	661.3
	s	0.1365	0.1983	0.2566	0.3120	0.3646	0.4150	1.642
6.0	v	1.0077	1.0168	1.0287	1.0432	1.0601	1.0797	0.323
	i	40.1	60.1	80.1	100.1	120.3	140.7	659.4
	s	0.1365	0.1983	0.2566	0.3120	0.3646	0.4150	1.618
7.0	v	1.0076	1.0168	1.0286	1.0432	1.0600	1.0796	1.102
	i	40.1	60.1	80.1	100.1	120.3	140.7	161.3
	s	0.1365	0.1983	0.2566	0.3120	0.3646	0.4150	0.463

180°	200°	220°	240°	260°	280°	300°	t / p, kg per sqcm	
2.652	2.771	2.890	3.009	3.127	3.246	3.364	v	0.80
677.5	686.9	696.3	705.5	715.2	724.8	734.4	i	
1.8769	1.8971	1.9165	1.9351	1.9531	1.9706	1.9876	s	
2.356	2.462	2.568	2.673	2.779	2.884	2.989	v	0.90
677.3	686.7	696.1	705.6	715.1	724.7	734.3	i	
1.8637	1.8839	1.9033	1.9220	1.9400	1.9575	1.9745	s	
2.119	2.214	2.310	2.405	2.500	2.595	2.690	v	1.0
677.2	686.6	696.0	705.5	714.9	724.5	734.0	i	
1.8515	1.8717	1.8913	1.9101	1.9284	1.9461	1.9634	s	
1.763	1.843	1.923	2.002	2.082	2.161	2.240	v	1.2
676.9	686.4	695.8	705.3	714.8	724.3	733.9	i	
1.8310	1.8514	1.8710	1.8898	1.9079	1.9258	1.9431	s	
1.509	1.578	1.647	1.715	1.783	1.851	1.919	v	1.4
676.7	686.1	695.6	705.1	714.6	724.2	733.8	i	
1.8136	1.8340	1.8536	1.8725	1.8909	1.9086	1.9259	s	
1.319	1.379	1.439	1.499	1.559	1.619	1.678	v	1.6
676.4	685.9	695.4	704.9	714.4	724.0	733.6	i	
1.7984	1.8188	1.8386	1.8576	1.8759	1.8936	1.9109	s	
1.171	1.225	1.278	1.332	1.385	1.438	1.491	v	1.8
676.1	685.7	695.2	704.7	714.3	723.9	733.5	i	
1.7852	1.8056	1.8252	1.8442	1.8626	1.8804	1.8977	s	
1.052	1.101	1.149	1.197	1.245	1.293	1.341	v	2.0
675.9	685.4	695.0	704.5	714.1	723.8	733.4	i	
1.7732	1.7937	1.8133	1.8324	1.8509	1.8687	1.8858	s	
0.8399	0.8790	0.9179	0.9567	0.9953	1.033	1.071	v	2.5
675.2	684.8	694.4	704.0	713.7	723.4	733.0	i	
1.7475	1.7683	1.7882	1.8072	1.8256	1.8435	1.8609	s	
0.6975	0.7304	0.7631	0.7956	0.8281	0.8603	0.8923	v	3.0
674.5	684.2	693.9	703.6	713.2	723.0	732.7	i	
1.7263	1.7471	1.7671	1.7864	1.8048	1.8227	1.8402	s	
0.5197	0.5448	0.5697	0.5944	0.6190	0.6433	0.6676	v	4.0
673.2	683.0	692.8	702.6	712.4	722.5	732.1	i	
1.6927	1.7139	1.7341	1.7535	1.7723	1.7904	1.8079	s	
0.4129	0.4334	0.4537	0.4736	0.4935	0.5131	0.5327	v	5.0
671.7	681.7	691.7	701.6	711.5	721.5	731.4	i	
1.6659	1.6875	1.7079	1.7277	1.7467	1.7649	1.7826	s	
0.3416	0.3591	0.3763	0.3932	0.4099	0.4264	0.4428	v	6.0
670.1	680.6	690.7	700.7	710.7	720.7	730.7	i	
1.6431	1.6655	1.6864	1.7061	1.7254	1.7438	1.7616	s	
0.2906	0.3059	0.3209	0.3356	0.3501	0.3644	0.3785	v	7.0
668.8	679.4	689.7	699.8	709.9	720.0	730.1	i	
1.6235	1.6467	1.6680	1.6882	1.7075	1.7260	1.7438	s	

p, kg per sqcm		t 40°	60°	80°	100°	120°	140°	160°
8.0	v	1.0076	1.0167	1.0286	1.0431	1.0600	1.0795	1.102
	i	40.2	60.1	80.1	100.2	120.3	140.7	161.3
	s	0.1365	0.1983	0.2566	0.3119	0.3646	0.4149	0.463
9.0	v	1.0075	1.0167	1.0285	1.0431	1.0599	1.0795	1.101
	i	40.2	60.1	80.1	100.2	120.4	140.7	161.3
	s	0.1364	0.1983	0.2565	0.3119	0.3645	0.4149	0.463
10	v	1.0075	1.0166	1.0285	1.0430	1.0599	1.0794	1.101
	i	40.2	60.1	80.1	100.2	120.4	140.7	161.3
	s	0.1364	0.1982	0.2565	0.3119	0.3645	0.4149	0.463
12	v	1.0074	1.0165	1.0284	1.0429	1.0598	1.0793	1.101
	i	40.2	60.2	80.2	100.2	120.4	140.8	161.3
	s	0.1364	0.1982	0.2565	0.3119	0.3645	0.4148	0.463
14	v	1.0073	1.0164	1.0283	1.0428	1.0596	1.0792	1.101
	i	40.3	60.2	80.2	100.3	120.4	140.8	161.4
	s	0.1364	0.1982	0.2564	0.3118	0.3644	0.4148	0.463
16	v	1.0072	1.0163	1.0282	1.0427	1.0595	1.0791	1.101
	i	40.3	60.2	80.2	100.3	120.5	140.8	161.4
	s	0.1364	0.1982	0.2564	0.3118	0.3644	0.4147	0.463
18	v	1.0071	1.0162	1.0281	1.0425	1.0594	1.0789	1.101
	i	40.4	60.3	80.3	100.3	120.5	140.9	161.4
	s	0.1364	0.1982	0.2564	0.3117	0.3644	0.4147	0.463
20	v	1.0070	1.0161	1.0280	1.0425	1.0593	1.0788	1.101
	i	40.4	60.3	80.3	100.4	120.5	140.9	161.4
	s	0.1364	0.1981	0.2563	0.3117	0.3643	0.4146	0.463
25	v	1.0068	1.0159	1.0278	1.0422	1.0591	1.0785	1.100
	i	40.5	60.4	80.4	100.5	120.6	141.0	161.5
	s	0.1363	0.1980	0.2562	0.3116	1.3642	1.4145	0.463
30	v	1.0066	1.0157	1.0275	1.0419	1.0588	1.0782	1.100
	i	40.6	60.5	80.5	100.5	120.7	141.1	161.6
	s	0.1362	0.1980	0.2561	0.3115	0.3641	0.4144	0.462
35	v	1.0064	1.0155	1.0273	1.0417	1.0585	1.0779	1.100
	i	40.7	60.6	80.6	100.6	120.8	141.1	161.6
	s	0.1362	0.1979	0.2561	0.3114	0.3640	0.4142	0.462
40	v	1.0062	1.0152	1.0271	1.0414	1.0582	1.0776	1.099
	i	40.8	60.7	80.7	100.7	120.9	141.2	161.7
	s	0.1362	0.1978	0.2560	0.3113	0.3639	0.4142	0.462
45	v	1.0060	1.0150	1.0269	1.0412	1.0580	1.0773	1.099
	i	40.9	60.8	80.8	100.8	121.0	141.3	161.8
	s	0.1361	0.1978	0.2559	0.3112	0.3638	0.4141	0.462
50	v	1.0057	1.0148	1.0266	1.0409	1.0577	1.0770	1.099
	i	41.0	60.9	80.9	100.9	121.1	141.4	161.8
	s	0.1361	0.1977	0.2558	0.3111	0.3637	0.4140	0.462

180°	200°	220°	240°	260°	280°	300°.	t / p, kg per sqcm	
0.2524	0.2662	0.2795	0.2925	0.3054	0.3180	0.3305	*v*	8.0
667.3	678.2	688.7	699.0	709.2	719.4	729.4	*i*	
1.6063	1.6300	1.6517	1.6722	1.6916	1.7102	1.7282	*s*	
0.2226	0.2353	0.2472	0.2589	0.2704	0.2818	0.2930	*v*	9.0
665.5	676.8	687.5	698.0	708.5	718.6	728.7	*i*	
1.5905	1.6147	1.6369	1.6577	1.6776	1.6964	1.7144	*s*	
0.1987	0.2103	0.2214	0.2321	0.2425	0.2529	0.2630	*v*	10
663.8	675.4	686.5	697.2	707.6	717.8	728.0	*i*	
1.5760	1.6008	1.6236	1.6449	1.6650	1.6839	1.7019	*s*	
1.1273	0.1728	0.1825	0.1918	0.2007	0.2095	0.2181	*v*	12
182.3	672.9	684.5	695.3	705.9	716.4	726.7	*i*	
0.5106	1.5762	1.6000	1.6220	1.6425	1.6618	1.6802	*s*	
1.1272	0.1460	0.1547	0.1629	0.1708	0.1784	0.1859	*v*	14
182.3	670.0	682.3	693.5	704.2	714.6	725.1	*i*	
0.5105	1.5545	1.5796	0.6020	1.6229	1.6426	1.6612	*s*	
1.1270	1.1565	0.1338	0.1411	0.1482	0.1551	0.1618	*v*	16
182.3	203.6	679.9	691.4	702.3	713.2	724.0	*i*	
0.5104	0.5562	1.5610	1.5843	1.6056	1.6257	1.6447	*s*	
1.1268	1.1563	0.1175	0.1242	0.1307	0.1369	0.1430	*v*	18
182.3	203.6	677.0	689.3	700.6	711.8	722.8	*i*	
0.5103	0.5561	1.5438	1.5681	1.5900	1.6104	1.6298	*s*	
1.1267	1.1561	0.1043	0.1108	0.1168	0.1225	0.1281	*v*	20
182.3	203.6	674.4	687.2	698.9	710.2	721.3	*i*	
0.5102	0.5560	1.5280	1.5530	1.5756	1.5967	1.6166	*s*	
1.1263	1.1556	1.1899	0.08643	0.09158	0.09640	0.1010	*v*	25
82.3	203.6	225.4	681.4	694.1	706.2	717.8	*i*	
0.5100	0.5558	0.6009	1.5200	1.5443	1.5665	1.5874	*s*	
1.1259	1.1552	1.1892	0.06987	0.07459	0.07889	0.08294	*v*	30
82.4	203.6	225.4	675.0	688.9	702.9	714.2	*i*	
0.5098	0.5556	0.6006	1.4900	1.5167	1.5405	1.5624	*s*	
1.1255	1.1547	1.1886	1.2290	0.06234	0.06630	0.06998	*v*	35
82.5	203.7	225.4	247.8	683.8	697.7	710.5	*i*	
0.5096	0.5553	0.6004	0.6448	1.4919	1.5173	1.5404	*s*	
1.1251	1.1542	1.1880	1.2282	0.05302	0.05679	0.06022	*v*	40
82.5	203.7	225.4	247.8	678.0	693.0	706.6	*i*	
0.5094	0.5551	0.6001	0.6445	1.4684	1.4957	1.5201	*s*	
1.1247	1.1537	1.1874	1.2274	0.04567	0.04935	0.05260	*v*	45
82.6	203.8	225.4	247.8	671.6	687.9	702.5	*i*	
0.5092	0.5549	0.5999	0.6442	1.4458	1.4757	1.5017	*s*	
1.1243	1.1532	1.1868	1.2266	0.2751	0.04330	0.04646	*v*	50
82.6	203.8	225.5	247.8	271.1	682.7	698.4	*i*	
0.5090	0.5547	0.5996	0.6439	0.6885	1.4564	1.4842	*s*	

p, kg per sqcm		t 40°	60°	80°	100°	120°	140°	160
60	v	1.0053	1.0144	1.0262	1.0404	1.0572	1.0764	1.0
	i	41.2	61.1	81.1	101.1	121.2	141.5	162.0
	s	0.1360	0.1976	0.2556	0.3109	0.3635	0.4137	0.4
70	v	1.0049	1.0139	1.0257	1.0399	1.0566	1.0758	1.0
	i	41.4	61.3	81.2	101.2	121.4	141.7	162.1
	s	0.1359	0.1974	0.2555	0.3107	0.3633	0.4135	0.4
80	v	1.0045	1.0135	1.0252	1.0394	1.0561	1.0752	0.0
	i	41.6	61.5	81.4	101.4	121.6	141.8	162.2
	s	0.1359	0.1973	0.2553	0.3105	0.3631	0.4133	0.4
90	v	1.0040	1.0130	1.0248	1.0389	1.0556	1.0746	1.0
	i	41.8	61.7	81.6	101.6	121.7	142.0	162.4
	s	0.1357	0.1971	0.2551	0.3103	0.3628	0.4130	0.4
100	v	1.0036	1.0126	1.0243	1.0384	1.0550	1.0740	1.0
	i	42.1	61.9	81.8	101.8	121.9	142.1	162.5
	s	0.1356	0.1970	0.2550	0.3101	0.3626	0.4128	0.4
120	v	1.0028	1.0117	1.0234	1.0375	1.0540	1.0728	1.0
	i	42.5	62.3	82.2	102.1	122.2	142.4	162.8
	s	0.1355	0.1967	0.2547	0.3097	0.3623	0.4124	0.4
140	v	1.0019	1.0109	1.0225	1.0365	1.0529	1.0717	1.0
	i	42.9	62.7	82.5	102.5	122.6	142.8	163.1
	s	0.1352	0.1965	0.2544	0.3094	0.3619	0.4119	0.4
160	v	1.0011	1.0100	1.0216	1.0356	1.0519	1.0705	1.0
	i	43.3	63.1	82.9	102.9	122.9	143.1	163.4
	s	0.1351	0.1962	0.2541	0.3090	0.3615	0.4115	0.4
180	v	1.0003	1.0092	1.0207	1.0347	1.0508	1.0694	1.0
	i	43.7	63.5	83.3	103.2	123.2	143.3	163.6
	s	0.1350	0.1959	0.2538	0.3087	0.3611	0.4110	0.4
200	v	0.9995	1.0083	1.0198	1.0337	1.0498	1.0682	1.0
	i	44.1	63.8	83.7	103.6	123.6	143.7	163.9
	s	0.1347	0.1956	0.2534	0.3084	0.3607	0.4106	0.4
220	v	0.9986	1.0075	1.0190	1.0328	1.0488	1.0671	1.0
	i	44.5	64.2	84.0	103.9	123.9	144.0	164.2
	s	0.1345	0.1953	0.2531	0.3080	0.3602	0.4101	0.4
240	v	0.9978	1.0067	1.0181	1.0318	1.0478	1.0661	1.0
	i	44.9	64.6	84.4	104.3	124.3	144.3	164.5
	s	0.1344	0.1951	0.2528	0.3076	0.3598	0.4097	0.4

Continued

180°	200°	220°	240°	260°	280°	300°	t / p_i kg per sqcm	
1.1235	1.1522	1.1857	1.2251	1.2729	0.03405	0.03711	v	60
182.8	203.9	225.5	247.8	270.9	671.0	689.0	i	
0.5086	0.5543	0.5991	0.6433	0.6878	1.4188	1.4512	s	
1.1226	1.1513	1.1845	1.2236	1.2709	1.3308	0.03029	v	70
182.9	204.0	225.6	247.8	270.9	295.2	678.7	i	
0.5082	0.5539	0.5986	0.6428	0.6871	0.7317	1.4195	s	
1.1219	1.1504	1.1833	1.2221	1.2689	1.3279	0.02503	v	80
183.0	204.1	225.7	247.8	270.9	295.1	667.0	i	
0.5079	0.5535	0.5982	0.6423	0.6864	0.7308	1.3875	s	
1.1211	1.1494	1.1822	1.2206	1.2669	1.3250	1.4024	v	90
183.1	204.2	225.7	247.9	270.9	295.0	321.1	i	
0.5075	0.5532	0.5977	0.6417	0.6858	0.7300	0.7764	s	
1.1203	1.1485	1.1810	1.2192	1.2650	1.3222	1.3979	v	100
183.2	204.3	225.8	247.9	270.9	294.9	320.7	i	
0.5072	0.5527	0.5973	0.6412	0.6852	0.7293	0.7751	s	
1.1188	1.1466	1.1788	1.2163	1.2613	1.3169	1.3897	v	120
183.5	204.5	225.9	248.0	270.8	294.6	320.1	i	
0.5066	0.5520	0.5964	0.6402	0.6839	0.7278	0.7729	s	
1.1172	1.1448	1.1766	1.2136	1.2576	1.3118	1.3820	v	140
183.7	204.7	226.1	248.0	270.8	294.5	319.5	i	
0.5060	0.5513	0.5955	0.6392	0.6827	0.7263	0.7709	s	
1.1157	1.1430	1.1744	1.2108	1.2541	1.3070	1.3746	v	160
183.9	204.9	226.2	248.1	270.7	294.4	319.1	i	
0.5054	0.5506	0.5946	0.6382	0.6816	0.7250	0.7690	s	
1.1143	1.1412	1.1722	1.2082	1.2506	1.3023	1.3678	v	180
184.2	205.1	226.3	248.2	270.7	294.2	318.7	i	
0.5048	0.5499	0.5938	0.6372	0.6804	0.7236	0.7673	s	
1.1128	1.1395	1.1701	1.2055	1.2472	1.2977	1.3612	v	200
184.4	205.3	226.5	248.2	270.7	294.0	318.4	i	
0.5046	0.5493	0.5932	0.6366	0.6793	0.7222	0.7656	s	
1.1113	1.1379	1.1680	1.2029	1.2439	1.2933	1.3549	v	220
184.7	205.4	226.2	248.3	270.7	293.9	318.0	i	
0.5040	0.5487	0.5924	0.6357	0.6783	0.7209	0.7640	s	
1.1099	1.1362	1.1660	1.2005	1.2408	1.2891	1.3489	v	240
184.9	205.6	226.8	248.5	270.7	293.9	317.9	i	
0.5035	0.5481	0.5917	0.6348	0.6773	0.7196	0.7625	s	

p, kg per sqcm \ t		40°	60°	80°	100°	120°	140°	160°
260	v	0.9970	1.0058	1.0172	1.0309	1.0468	1.0649	1.08
	i	45.3	65.0	84.8	104.6	124.6	144.6	164.8
	s	0.1342	0.1949	0.2525	0.3073	0.3594	0.4092	0.45
280	v	0.9962	1.0050	1.0164	1.0300	1.0458	1.0639	1.08
	i	45.8	65.4	85.2	105.0	124.9	144.9	165.1
	s	0.1340	0.1947	0.2522	0.3069	0.3590	0.4088	0.45
300	v	0.9954	1.0042	1.0156	1.0292	1.0449	1.0627	1.08
	i	46.2	65.8	85.5	105.3	125.3	145.3	165.5
	s	0.1338	0.1945	0.2520	0.3066	0.3587	0.4084	0.45
320	v	0.9946	1.0034	1.0146	1.0282	1.0439	1.0615	1.08
	i	46.6	66.2	85.9	105.8	126.6	145.6	165.8
	s	0.1336	0.1942	0.2516	0.3062	0.3582	0.4079	0.45
340	v	0.9938	1.0026	1.0138	1.0274	1.0429	1.0604	1.08
	i	47.0	66.6	86.3	106.0	126.0	145.9	166.0
	s	0.1334	0.1940	0.2514	0.3059	0.3577	0.4074	0.45
360	v	0.9931	1.0019	1.0131	1.0265	1.0420	1.0595	1.07
	i	47.4	67.0	86.7	106.4	126.3	146.2	166.3
	s	0.1332	0.1937	0.2511	0.3055	0.3573	0.4069	0.45
380	v	0.9923	1.0011	1.0122	1.0256	1.0409	1.0583	1.07
	i	47.9	67.4	87.1	106.8	126.7	146.6	166.6
	s	0.1330	0.1935	0.2509	0.3052	0.3569	0.4065	0.45
400	v	0.9915	1.0004	1.0115	1.0248	1.0401	1.0574	1.07
	i	48.3	67.8	87.5	107.1	127.0	146.9	166.9
	s	0.1328	0.1933	0.2507	0.3049	0.3565	0.4061	0.45
420	v	0.9907	0.9996	1.0106	1.0238	1.0390	1.0562	1.07
	i	48.7	68.2	87.8	107.5	127.3	147.2	167.2
	s	0.1326	0.1931	0.2503	0.3045	0.3561	0.4056	0.45
440	v	0.9899	0.9988	1.0098	1.0230	1.0381	1.0552	1.07
	i	49.1	68.6	88.2	107.8	127.7	147.5	167.6
	s	0.1324	0.1929	0.2500	0.3041	0.3557	0.4052	0.45
460	v	0.9892	0.9981	1.0091	1.0221	1.0372	1.0541	1.07
	i	49.5	69.0	88.6	108.2	128.0	147.9	167.9
	s	0.1322	0.1926	0.2497	0.3038	0.3554	0.4047	0.45
480	v	0.9884	0.9973	1.0082	1.0212	1.0362	1.0530	1.07
	i	49.9	69.4	89.0	108.5	128.4	148.2	168.1
	s	0.1320	0.1924	0.2495	0.3035	0.3550	0.4043	0.45
500	v	0.9876	0.9966	1.0075	1.0204	1.0354	1.0521	1.07
	i	50.3	69.8	89.3	108.9	128.7	148.5	168.4
	s	0.1318	0.1922	0.2493	0.3032	0.3546	0.4039	0.45

180°	200°	220°	240°	260°	280°	300°	t / p, kg per sqcm	
1.1085	1.1345	1.1640	1.1980	1.2376	1.2850	1.3433	v	260
185.2	205.9	227.0	248.6	270.8	293.8	317.7	i	
0.5030	0.5475	0.5910	0.6339	0.6763	0.7182	0.7607	s	
1.1071	1.1328	1.1621	1.1956	1.2347	1.2811	1.3380	v	280
185.5	206.2	227.1	248.7	270.9	293.8	317.5	i	
0.5024	0.5469	0.5903	0.6331	0.6753	0.7171	0.7594	s	
1.1056	1.1313	1.1603	1.1934	1.2316	1.2772	1.3326	v	300
185.9	206.4	227.3	248.9	271.0	293.8	317.4	i	
0.5018	0.5463	0.5897	0.6323	0.6744	0.7160	0.7580	s	
1.1041	1.1297	1.1583	1.1910	1.2286	1.2734	1.3276	v	320
186.2	206.6	227.5	249.1	271.1	293.8	317.2	i	
0.5012	0.5457	0.5890	0.6315	0.6735	0.7150	0.7567	s	
1.1027	1.1281	1.1565	1.1890	1.2258	1.2698	1.3227	v	340
186.4	207.0	227.8	249.2	271.1	293.8	312.2	i	
0.5007	0.5451	0.5884	0.6308	0.6726	0.7140	0.7554	s	
1.1013	1.1265	1.1547	1.1868	1.2231	1.2663	1.3180	v	360
186.7	207.4	228.0	249.3	271.3	293.8	317.0	i	
0.5002	0.5445	0.5877	0.6301	0.6717	0.7129	0.7541	s	
1.0999	1.1249	1.1529	1.1847	1.2206	1.2630	1.3135	v	380
187.0	207.4	228.2	249.5	271.3	293.8	316.9	i	
0.4997	0.5439	0.5871	0.6293	0.6707	0.7118	0.7529	s	
1.0986	1.1234	1.1513	1.1827	1.2183	1.2598	1.3091	v	400
187.3	207.7	228.4	249.7	271.5	293.9	316.8	i	
0.4992	0.5434	0.5865	0.6286	0.6699	0.7108	0.7517	s	
1.0972	1.1218	1.1496	1.1806	1.2160	1.2569	1.3050	v	420
187.6	208.0	228.6	249.8	271.6	293.9	316.8	i	
0.4986	0.5428	0.5858	0.6278	0.6690	0.7097	0.7506	s	
1.0959	1.1203	1.1479	1.1787	1.2138	1.2541	1.3010	v	440
187.8	208.2	228.8	249.9	271.7	293.9	316.7	i	
0.4981	0.5422	0.5851	0.6270	0.6682	0.7087	0.7494	s	
1.0947	1.1189	1.1463	1.1769	1.2117	1.2512	1.2972	v	460
188.0	208.4	228.9	250.0	271.7	293.9	316.6	i	
0.4976	0.5416	0.5844	0.6263	0.6673	0.7077	0.7483	s	
1.0934	1.1175	1.1447	1.1751	1.2095	1.2485	1.2936	v	480
188.3	208.6	229.1	250.2	271.8	293.9	316.5	i	
0.4971	0.5410	0.5837	0.6255	0.6664	0.7067	0.7471	s	
1.0922	1.1161	1.1431	1.1733	1.2075	1.2461	1.2902	v	500
188.6	208.8	229.3	250.4	271.9	293.9	316.4	i	
0.4965	0.5404	0.5831	0.6248	0.6656	0.7056	0.7459	s	

p, kg per sqcm		t 320°	340°	360°	380°	400°	420°	440°
0.05	v	55.80	57.69	59.57	61.46	63.33	65.21	67.09
	i	744.4	754.0	763.8	773.6	783.4	793.3	803.3
	s	2.3102	2.3261	2.3418	2.3569	2.3717	2.3863	2.400(
0.06	v	46.50	48.07	49.64	51.20	52.78	54.35	55.92
	i	744.4	754.0	763.8	773.6	783.4	793.3	803.3
	s	2.2900	2.3059	2.3216	2.3368	2.3516	2.3662	2.380!
0.08	v	34.88	36.05	37.23	38.41	39.59	40.76	41.94
	i	744.4	754.0	763.8	773.6	783.4	793.3	803.3
	s	2.2582	2.2742	2.2898	2.3049	2.3198	2.3343	2.348(
0.10	v	27.90	28.84	29.78	30.72	31.67	32.61	33.55
	i	744.4	754.0	763.8	773.6	783.4	793.3	803.3
	s	2.2337	2.2497	2.2652	2.2804	2.2953	2.3098	2.324(
0.12	v	23.25	24.03	24.82	25.60	26.39	27.17	27.95
	i	744.4	754.0	763.8	773.6	783.4	793.3	803.3
	s	2.2135	2.2295	2.2451	2.2603	2.2752	2.2897	2.304(
0.16	v	17.43	18.02	18.61	19.20	19.79	20.37	20.96
	i	744.4	754.0	763.8	773.6	783.4	793.3	803.3
	s	2.1819	2.1978	2.2133	2.2286	2.2435	2.2580	2.272!
0.20	v	13.95	14.42	14.89	15.36	15.83	16.30	16.77
	i	744.4	754.0	763.8	773.6	783.4	793.3	803.3
	s	2.1573	2.1732	2.1887	2.2040	2.2189	2.2334	2.247(
0.24	v	11.62	12.02	12.41	12.80	13.19	13.59	13.98
	i	744.3	754.0	763.8	773.6	783.4	793.3	803.3
	s	2.1371	2.1531	2.1686	2.1839	2.1988	2.2133	2.227!
0.30	v	9.298	9.612	9.926	10.24	10.55	10.87	11.18
	i	744.3	754.0	763.8	773.6	783.4	793.3	803.3
	s	2.1124	2.1285	2.1441	2.1592	2.1741	2.1887	2.203(
0.40	v	6.971	7.207	7.443	7.679	7.916	8.151	8.387
	i	744.3	753.9	763.7	773.5	783.3	793.2	803.2
	s	2.0807	2.0968	2.1124	2.1276	2.1425	2.1571	2.171(
0.50	v	5.577	5.767	5.955	6.144	6.333	6.521	6.710
	i	744.2	753.9	763.7	773.5	783.3	793.2	803.2
	s	2.0560	2.0721	2.0876	2.1029	2.1177	2.1323	2.146!
0.60	v	4.646	4.804	4.961	5.118	5.277	5.434	5.591
	i	744.1	753.8	763.6	773.4	783.3	793.2	803.2
	s	2.0359	2.0519	2.0675	2.0827	2.0976	2.1122	2.126!
0.70	v	3.982	4.117	4.252	4.388	4.522	4.657	4.792
	i	744.1	753.8	763.6	773.4	783.2	793.1	803.1
	s	2.0189	2.0349	2.0504	2.0657	2.0806	2.0951	2.109(

Continued

460°	480°	500°	520°	550°	600°	700°	t / p, kg per sqcm	
68.98	70.86	72.74	74.62	77.45	82.17	91.58	v	0.05
813.3	823.4	833.6	843.8	859.3	885.5	938.9	i	
2.4146	2.4283	2.4417	2.4550	2.4745	2.5057	2.5637	s	
57.48	59.05	60.62	62.18	64.55	68.47	76.32	v	0.06
813.3	823.4	833.6	843.8	859.3	885.5	938.9	i	
2.3945	2.4082	3.4217	2.4349	2.4544	2.4836	2.5436	s	
43.12	44.30	45.47	46.65	48.41	51.35	57.24	v	0.08
813.3	823.4	833.6	843.8	859.3	885.4	938.9	i	
2.3626	2.3764	2.3899	2.4031	2.4226	2.4539	2.5119	s	
34.49	35.43	36.38	37.32	38.73	41.08	45.79	v	0.10
813.3	823.4	833.6	843.8	859.3	885.4	938.9	i	
2.3381	2.3519	2.3654	2.3786	2.3980	2.4293	2.4873	s	
28.74	29.52	30.31	31.10	32.27	34.24	38.16	v	0.12
813.3	823.4	833.6	843.8	859.3	885.4	938.9	i	
2.3181	2.3318	2.3453	2.3585	2.3780	2.4092	2.4672	s	
21.54	22.13	22.72	23.31	24.20	25.68	28.62	v	0.16
813.3	823.4	833.6	843.8	859.3	885.4	938.9	i	
2.2863	2.3001	2.3137	2.3271	2.3466	2.3775	2.4355	s	
17.23	17.70	18.17	18.64	19.35	20.54	22.89	v	0.20
813.3	823.4	833.6	843.8	859.3	885.4	938.9	i	
2.2617	2.2755	2.2891	2.3025	2.3220	2.3529	2.4109	s	
14.37	14.76	15.16	15.55	16.14	17.12	19.08	v	0.24
813.3	823.4	833.6	843.8	859.3	885.4	938.9	i	
2.2416	2.2554	2.2690	2.2824	2.3019	2.3329	2.3908	s	
11.50	11.81	12.12	12.44	12.91	13.69	15.262	v	0.30
813.3	823.4	833.6	843.8	859.3	885.4	938.9	i	
2.2171	2.2309	2.2445	2.2579	2.2773	2.3082	2.3662	s	
8.623	8.858	9.093	9.329	9.682	10.269	11.446	v	0.40
813.2	823.4	833.6	843.8	859.3	885.4	938.9	i	
2.1855	2.1993	2.2128	2.2261	2.2456	2.2765	2.3345	s	
6.898	7.087	7.275	7.464	7.746	8.215	9.157	v	0.50
813.2	823.3	833.5	843.7	859.3	885.4	938.8	i	
2.1607	2.1745	2.1880	2.2014	2.2209	2.2519	2.3099	s	
5.750	5.906	6.063	6.220	6.454	6.846	7.630	v	0.60
813.2	823.3	833.5	843.7	859.2	885.4	938.8	i	
2.1495	2.1542	2.1678	2.1811	2.2007	2.2318	2.2899	s	
4.927	5.061	5.196	5.331	5.532	5.867	6.540	v	0.70
813.1	823.3	833.5	843.7	859.2	885.3	938.8	i	
2.1235	2.1372	2.1508	2.1641	2.1837	2.2148	2.2728	s	

p, kg per sqcm		t 320°	340°	360°	380°	400°	420°	440°
0.80	v	3.482	3.601	3.720	3.838	3.956	4.074	4.191
	i	744.0	753.7	763.5	773.3	783.2	793.1	803.1
	s	2.0039	2.0199	2.0856	2.0508	2.0657	2.0803	2.094
0.90	v	3.095	3.200	3.305	3.410	3.515	3.620	3.725
	i	743.9	753.6	763.4	773.2	783.1	793.1	803.1
	s	1.9908	2.0063	2.0226	2.0377	2.0526	2.0671	2.081
1.0	v	2.784	2.880	2.975	3.068	3.163	3.257	3.352
	i	743.6	753.2	762.9	772.7	782.6	792.6	802.6
	s	1.9800	1.9961	2.0271	2.0271	2.0421	2.0567	2.070
1.2	v	2.320	2.399	2.478	2.556	2.635	2.713	2.792
	i	743.5	753.2	762.9	772.7	782.6	792.6	802.6
	s	1.9598	1.9759	1.9916	2.0069	2.0218	2.0366	2.050
1.4	v	1.987	2.056	2.123	2.190	2.258	2.325	2.393
	i	743.4	753.2	762.9	772.7	782.6	792.6	802.6
	s	1.9426	1.9587	1.9744	1.9898	2.0048	2.0194	2.033
1.6	v	1.738	1.798	1.857	1.916	1.975	2.034	2.093
	i	743.3	753.1	762.9	772.7	782.6	792.6	802.6
	s	1.9276	1.9439	1.9596	1.9749	1.9899	2.0046	2.018
1.8	v	1.545	1.598	1.650	1.702	1.755	1.807	1.860
	i	743.2	753.0	762.8	772.7	782.6	792.6	802.6
	s	1.9145	1.9308	1.9465	1.9618	1.9768	1.9915	2.005
2.0	v	1.389	1.437	1.485	1.532	1.579	1.627	1.673
	i	743.1	753.0	762.8	772.7	782.6	792.6	802.6
	s	1.9027	1.9190	1.9349	1.9503	1.9652	1.9799	1.994
2.5	v	1.111	1.149	1.187	1.225	1.262	1.300	1.338
	i	742.8	752.7	762.5	772.5	782.4	792.4	802.5
	s	1.8778	1.8941	1.9100	1.9255	1.9404	1.9551	1.969
3.0	v	0.9243	0.9562	0.9881	1.020	1.052	1.083	1.115
	i	742.5	752.5	762.3	772.2	782.2	792.2	802.3
	s	1.8572	1.8737	1.8896	1.9051	1.9200	1.9347	1.949
4.0	v	0.6917	0.7158	0.7398	0.7637	0.7875	0.8114	0.835
	i	742.0	751.9	761.8	771.8	781.8	791.8	802.0
	s	1.8248	1.8413	1.8573	1.8728	1.8879	1.9026	1.917
5.0	v	0.5521	0.3715	0.5908	0.6101	0.6294	0.6485	0.667
	i	741.4	751.4	761.4	771.4	781.5	791.5	801.8
	s	1.7996	1.8161	1.8322	1.8478	1.8630	1.8778	1.892
6.0	v	0.4591	0.4753	0.4915	0.5077	0.5237	0.5398	0.555
	i	740.8	750.9	760.9	771.0	781.1	791.1	801.3
	s	1.7786	1.7953	1.8115	1.8271	1.8422	1.8571	1.871
7.0	v	0.3926	0.4066	0.4206	0.4345	0.4483	0.4621	0.475
	i	740.2	750.3	760.3	770.5	780.6	790.8	801.0
	s	1.7609	1.7776	1.7939	1.8097	1.8250	1.84399	1.854

460°	480°	500°	520°	550°	600°	700°	t / p, kg per sqcm	
4.309	4.427	4.545	4.663	4.840	5.134	5.722	v	0.80
813.1	823.3	833.5	843.7	859.2	885.3	938.8	i	
2.1086	2.1224	2.1360	2.1494	2.1690	2.2001	2.2581	s	
3.830	3.936	4.040	4.145	4.302	4.563	5.086	v	0.90
813.1	823.4	833.4	843.6	859.2	885.3	938.8	i	
2.0954	2.1092	2.1228	2.1362	2.1558	2.1871	2.2451	s	
3.446	3.540	3.635	3.729	3.871	4.107	4.578	v	1.0
812.6	822.8	833.0	843.2	858.8	884.8	938.0	i	
2.0848	2.0985	2.1119	2.1250	2.1443	2.1749	2.2325	s	
2.871	2.950	3.028	3.107	3.225	3.422	3.815	v	1.2
812.6	822.8	833.0	843.2	858.8	884.8	938.0	i	
2.0646	2.0783	2.0918	2.1049	2.1242	2.1548	2.2126	s	
2.460	2.528	2.595	2.662	2.765	2.933	3.269	v	1.4
812.6	822.8	833.0	843.2	858.8	884.8	938.0	i	
2.0476	2.0613	2.0748	2.0879	2.1072	2.1378	2.1954	s	
2.152	2.211	2.270	2.330	2.418	2.566	2.861	v	1.6
812.6	822.8	833.0	843.2	858.8	884.8	938.0	i	
2.0328	2.0464	2.0599	2.0730	2.0923	2.1229	2.1205	s	
1.913	1.965	2.018	2.071	2.150	2.281	2.543	v	1.8
812.6	822.8	833.0	843.2	858.8	884.8	938.0	i	
2.0198	2.0335	2.0469	2.0600	2.0793	2.1099	2.1675	s	
1.721	1.768	1.815	1.864	1.935	2.052	2.288	v	2.0
812.6	822.8	833.0	843.2	858.8	884.8	937.9	i	
2.0081	2.0218	2.0353	2.0484	2.0677	2.0983	2.1560	s	
1.376	1.414	1.453	1.490	1.547	1.642	1.831	v	2.5
812.5	822.7	832.9	843.1	858.7	884.7	937.8	i	
1.9837	1.9971	2.0105	2.0236	2.0429	2.0735	2.1313	s	
1.147	1.179	1.210	1.242	1.289	1.368	1.5250	v	3.0
812.3	822.5	832.7	842.9	858.5	884.5	937.7	i	
1.9631	1.9768	1.9903	2.0035	2.0228	2.0534	2.1112	s	
0.8590	0.8828	0.9066	0.9304	0.9660	1.025	1.1435	v	4.0
812.1	822.3	832.5	842.8	858.4	884.4	937.6	i	
1.9311	1.9448	1.9583	1.9715	1.9908	2.0215	2.0794	s	
0.6867	0.7058	0.7248	0.7439	0.7724	0.8198	0.9144	v	5.0
811.7	821.9	832.1	842.4	858.0	884.1	937.5	i	
1.9062	1.9200	1.9335	1.9467	1.9661	1.9968	2.0547	s	
0.5717	0.5876	0.6036	0.6194	0.6432	0.6829	0.7618	v	6.0
811.5	821.7	831.9	842.2	857.8	884.0	937.4	i	
1.8857	1.8996	1.9131	1.9263	1.9457	1.9764	2.0343	s	
0.4896	0.5033	0.5169	0.5306	0.5510	0.5851	0.6528	v	7.0
811.2	821.4	831.7	842.0	857.6	883.8	937.3	i	
1.8685	1.8824	1.8959	1.9091	1.9285	1.9594	2.0173	s	

p, kg per sqcm		t 320°	340°	360°	380°	400°	420°	440°
8.0	v	0.3429	0.3552	0.3674	0.3796	0.3918	0.4039	0.4159
	i	739.5	749.5	760.0	770.1	780.3	790.5	800.6
	s	1.7455	1.7623	1.7786	1.7945	1.8099	1.8248	1.8393
9.0	v	0.3040	0.3150	0.3260	0.3369	0.3477	0.3586	0.3693
	i	739.0	749.2	759.4	769.7	779.9	790.1	800.3
	s	1.7318	1.7487	1.7651	1.7810	1.7963	1.8114	1.8259
10	v	0.2731	0.2829	0.2929	0.3028	0.3126	0.3223	0.3320
	i	738.4	748.7	758.9	769.2	779.5	789.7	799.9
	s	1.7194	1.7365	1.7530	1.7690	1.7843	1.7996	1.8139
12	v	0.2265	0.2348	0.2432	0.2515	0.2598	0.2679	0.2761
	i	737.1	747.6	757.9	768.3	778.7	788.9	799.3
	s	1.6979	1.7151	1.7317	1.7478	1.7633	1.7784	1.7933
14	v	0.1933	0.2005	0.2077	0.2150	0.2220	0.2291	0.2361
	i	735.8	746.4	756.9	767.4	777.9	788.3	798.7
	s	1.6792	1.6966	1.7135	1.7297	1.7454	1.7607	1.7755
16	v	0.1683	0.1747	0.1811	0.1875	0.1937	0.2000	0.2062
	i	734.7	745.4	756.0	766.6	777.1	787.5	798.0
	s	1.6630	1.6807	1.6977	1.7140	1.7299	1.7453	1.7600
18	v	0.1490	0.1548	0.1605	0.1661	0.1717	0.1773	0.1829
	i	733.6	744.3	755.0	765.6	776.2	786.7	797.3
	s	1.6484	1.6663	1.6835	1.7000	1.7160	1.7315	1.7465
20	v	0.1334	0.1386	0.1438	0.1491	0.1542	0.1592	0.1642
	i	732.4	743.4	754.1	764.8	775.5	786.1	796.9
	s	1.6354	1.6534	1.6707	1.6874	1.7035	1.7190	1.7341
25	v	0.1055	0.1048	0.1141	0.1183	0.1225	0.1266	0.1308
	i	729.1	740.5	751.6	762.6	773.4	784.2	795.1
	s	1.6071	1.6256	1.6432	1.6603	1.6767	1.6924	1.7077
30	v	0.08680	0.09055	0.09421	0.09780	0.1013	0.1048	0.1084
	i	726.1	737.7	749.2	760.4	771.4	782.4	793.3
	s	1.5827	1.6019	1.6202	1.6376	1.6542	1.6703	1.6858
35	v	0.07344	0.07675	0.07997	0.08314	0.08624	0.08927	0.0922
	i	722.8	734.8	746.5	758.0	769.3	780.4	791.5
	s	1.5615	1.5812	1.6000	1.6180	1.6352	1.6513	1.6671
40	v	0.06338	0.06636	0.06927	0.7212	0.07490	0.07763	0.0803
	i	719.6	731.9	743.8	755.6	767.2	778.5	789.8
	s	1.5423	1.5631	1.5823	1.6003	1.6117	1.6345	1.6505
45	v	0.05556	0.05830	0.06095	0.06356	0.06610	0.06856	0.0709
	i	716.0	728.7	741.2	753.3	765.1	776.8	788.1
	s	1.5250	1.5463	1.5660	1.5848	1.6026	1.6194	1.6357
50	v	0.04927	0.05186	0.5432	0.05671	0.05904	0.06130	0.0635
	i	712.5	725.8	738.5	750.8	762.9	774.7	786.3
	s	1.5087	1.5308	1.5512	1.5703	1.5885	1.6057	1.6222

Continued

460°	480°	500°	520°	550°	600°	700°	t / p, kg per sqcm	
0.4280	0.4400	0.4519	0.4639	0.4819	0.5117	0.5711	v	8.0
810.8	821.0	831.4	841.8	857.4	883.6	937.1	i	
1.8534	1.8673	1.8808	1.8941	1.9135	1.9445	2.0026	s	
0.3800	0.3907	0.4014	0.4121	0 4280	0.4546	0.5074	v	9.0
810.5	820.8	831.2	841.6	857.2	883.4	936.9	i	
1.8402	1.8541	1.8677	1.8810	1.9004	1.9314	1.9895	s	
0.3417	0.3513	0.3609	0.3706	0.3851	0.4088	0.4565	v	10
810.2	820.5	830.9	841.3	856.9	883.2	936.8	i	
1.8282	1.8421	1.8558	1.8691	1.8885	1.9195	1.9711	s	
0.2842	0.2922	0.3003	0.3084	0.3205	0.3405	0.3802	v	12
809.7	820.1	830.5	840.9	856.5	882.8	936.5	i	
1.8076	1.8215	1.8351	1.8484	1.8679	1.9090	1.9574	s	
0.2431	0.2501	0.2570	0.2639	0.2744	0.2915	0.3257	v	14
809.1	819.5	829.9	840.3	856.0	882.5	936.3	i	
1.7898	1.8039	1.8177	1.8311	1.8406	1.8817	1.9402	s	
0.2123	0.2184	0.2245	0.2306	0.2398	0.2548	0.2848	v	16
808.4	818.8	829.4	839.8	855.6	882.1	936.0	i	
1.7745	1.7886	1.8024	1.8158	1.8353	1.8667	1.9253	s	
0.1884	0.1938	0.1992	0.2047	0.2129	0.2264	0.2529	v	18
807.7	818.2	828.8	839.3	855.2	881.7	936.6	i	
1.7610	1.7751	1.7889	0.8024	1.8220	1.8534	1.9121	s	
1.1692	0.1741	0.1790	0.1840	0.1913	0.2035	0.2276	v	20
807 1	817.7	828.3	838.8	854.7	881.3	935.5	i	
1.7486	1.7628	1.7767	1.7902	1.8100	1.8415	1.9013	s	
0.1347	0.1387	0.1426	0.1466	0.1527	0.1624	0.1818	v	25
805.7	816.3	827.0	837.6	853.7	880.5	934.8	i	
1.7225	1.7368	1.7509	1.7646	1.7844	1.8160	1.8752	s	
0.1118	0.1151	0.1185	0.1218	0.1269	0.1350	0.1512	v	30
804.1	814.9	825.7	836.5	852.6	879.6	934.1	i	
1.7008	1.7153	1.7295	1.7432	1 7632	1.7950	1.8545	s	
0.09525	0.09820	0.1011	0.1039	0.1083	0.1154	0.12949	v	35
802.5	813.5	824.4	835.3	851.5	878.7	933.4	i	
1.6822	1.6969	1.7112	1.7251	1.7452	1.7772	1.8370	s	
0.08293	0.08555	0.08816	0.09074	0.09457	0.1008	0.11313	v	40
801.0	812.0	823.0	834.0	850.4	877.7	932.7	i	
1.6659	1.6808	1.6953	1.7094	1.7296	1.7617	1.8217	s	
0.07337	0.07572	0.07804	0.08036	0.08380	0.08943	0.10041	v	45
801.0	812.0	823.0	834.0	850.4	877.7	932.7	i	
1.6659	1.6808	1.6953	1.7094	1.7296	1.7617	1.8217	s	
0.06571	0.06786	0.06999	0.07208	0.07519	0 08029	0.09020	v	50
797.7	809.1	820.3	831.5	848.2	875.8	931.3	i	
1.6380	1.6532	1.6681	1.6823	1.7029	1.7356	1.7961	s	

p, kgper sqcm \ t	320°	340°	360°	380°	400°	420°	440°
60	v 0.03976 i 705.1 s 1.4788	0.04213 719.6 1.5029	0.04432 733.1 1.5246	0.04642 746.1 1.5448	0.04845 758.7 1.5635	0.05052 770.9 1.5813	0.05233 782.7 1.5983
70	v 0.03287 i 697.1 s 1.4510	0.03512 713.0 1.4773	0.03714 727.0 1.5007	0.03903 741.0 1.5220	0.04084 754.1 1.5417	0.04260 766.8 1.5602	0.04430 779.1 1.5776
80	v 0.02757 i 688.0 s 1.4239	0.02976 705.8 1.4534	0.03171 721.5 1.4787	0.03348 735.9 1.5012	0.03514 749.5 1.5217	0.03674 762.6 1.5408	0.03828 775.3 1.5589
90	v 0.02336 i 677.7 s 1.3968	0.02553 698.0 1.4303	0.02745 715.1 1.4578	0.02914 730.4 1.4818	0.03070 744.6 1.5031	0.03218 758.3 1.5230	0.03359 771.4 1.5418
100	v 0.01988 i 666.0 s 1.3688	0.02210 689.2 1.4071	0.02397 708.0 1.4376	0.02560 724.6 1.4632	0.02709 739.8 1.4858	0.02848 754.1 1.5065	0.02981 767.8 1.5260
120	v 1.495 i 348.8 s 0.8225	0.01679 669.2 1.3594	0.01870 692.7 1.3978	0.02024 717.9 1.4282	0.02166 729.5 1.4537	0.02292 745.5 1.4765	0.02412 759.9 1.4975
140	v 1.481 i 347.5 s 0.8189	0.01253 642.8 1.3055	0.01471 674.4 1.3563	0.01634 698.0 1.3935	0.01772 718.2 1.4234	0.01893 736.1 1.4490	0.02004 751.5 1.4714
160	v 1.468 i 346.4 s 0.8159	1.621 379.4 0.8708	0.01154 651.8 1.3112	0.01331 681.9 1.3581	0.01471 705.6 1.3937	0.01590 725.8 1.4234	0.01696 742.6 1.4470
180	v 1.457 i 345.5 s 0.8133	1.596 376.9 0.8654	0.00862 620.3 1.2543	0.01083 662.8 1.3202	0.01231 691.6 1.3641	0.01351 714.3 1.3970	0.01454 733.2 1.4236
200	v 1.436 i 344.2 s 0.8110	1.554 373.5 0.8612	1.768 411.0 0.9280	0.00660 607.8 0.2770	0.00862 657.8 1.3327	0.00991 688.9 1.3710	0.01096 712.6 1.4008
220	v 1.436 i 344.2 s 0.8088	1.554 373.5 0.8578	1.768 411.0 0.9183	0.00660 607.8 1.2232	0.00862 657.8 1.2985	0.00991 688.9 1.3448	0.01096 712.6 1.3786
240	v 1.427 i 343.6 s 0.8067	1.538 372.2 0.8542	1.722 407.3 0.9108	0.00371 526.0 1.0937	0.00710 636.1 1.2606	0.00851 674.1 1.3168	0.00958 701.3 1.3562

460°	480°	500°	520°	550°	600°	700°	t / p, kg per sqcm	
0.05420	0.05604	0.05785	0.05962	0.06227	0.06658	0.07494	v	60
794.3	805.9	817.5	828.9	845.8	873.8	929.9	i	
1.6146	1.6302	1.6453	1.6598	1.6809	1.7138	1.7750	s	
0.04596	0.04759	0.04918	0.05073	0.05304	0.05678	0.06404	v	70
791.1	803.0	804.7	826.3	843.5	871.8	928.6	i	
1.5943	1.6103	1.6257	1.6404	1.6617	1.6951	1.7569	s	
0.03977	0.04122	0.04265	0.04405	0.04610	0.04944	0.05586	v	80
787.7	799.8	811.8	823.6	841.1	869.8	927.1	i	
1.5761	1.5925	1.6082	1.6233	1.6449	1.6788	1.7411	s	
0.03496	0.03629	0.03758	0.03884	0.04071	0.04372	0.04950	v	90
784.2	796.7	809.0	821.0	838.7	867.8	925.7	i	
1.5596	1.5766	1.5925	1.6078	1.6298	1.6642	1.7270	s	
0.03109	0.03232	0.03352	0.03469	0.03641	0.03916	0.04440	v	100
780.9	793.6	806.1	818.2	836.3	865.8	924.3	i	
1.5444	1.5617	1.5781	1.5938	1.6161	1.6509	1.7142	s	
0.02527	0.02635	0.02740	0.02842	0.02991	0.03229	0.03677	v	120
773.7	787.1	800.1	812.8	831.5	861.8	921.5	i	
1.5169	1.5351	1.5522	1.5685	1.5916	1.6273	1.6917	s	
0.02109	0.02208	0.02303	0.02394	0.02527	0.02738	0.03131	v	140
766.1	780.4	794.1	803.7	826.6	857.7	918.7	i	
1.4921	1.5112	1.5292	1.5463	1.5702	1.6067	1.6726	s	
0.01794	0.01887	0.01974	0.02058	0.02179	0.02369	0.02722	v	160
758.3	773.4	787.9	801.8	826.6	853.6	915.9	i	
1.4691	1.4895	1.5086	1.5262	1.5508	1.5886	1.6557	s	
0.01549	0.01636	0.01718	0.01796	0.01908	0.02083	0.02404	v	180
750.3	766.3	781.6	796.0	816.5	849.5	913.0	i	
1.4475	1.4691	1.4891	1.5075	1.5332	1.5720	1.6404	s	
0.01351	0.01436	0.01513	0.01587	0.01691	0.01854	0.02150	v	200
741.8	759.0	775.0	790.0	811.4	845.3	910.1	i	
1.4266	1.4498	1.4709	1.4903	1.5168	1.5567	1.6265	s	
0.01188	0.01270	0.01345	0.01414	0.01514	0.01666	0.01942	v	220
732.8	751.2	768.2	784.0	806.2	841.1	907.3	i	
1.4064	1.4313	1.4536	1.4739	1.5018	1.5428	1.6138	s	
0.01051	0.01131	0.01204	0.01271	0.01365	0.01510	0.01768	v	240
723.3	743.2	761.3	777.8	800.9	837.9	904.5	i	
1.3865	1.4130	1.4367	1.4584	1.4875	1.5295	1.6020	s	

p, kg per sqcm \ t		320°	340°	360°	380°	400°	420°	440°
260	v	1.418	1.523	1.688	0.00216	0.00565	0.00728	0.00840
	i	343.2	371.3	404.5	455.6	608.1	657.4	688.9
	s	0.8045	0.8513	0.9047	0.9837	1.2142	1.2869	1.3324
280	v	1.410	1.510	1.659	0.00199	0.00425	0.00618	0.00737
	i	342.8	370.4	402.3	446.2	572.1	638.9	675.2
	s	0.8028	0.8484	0.8998	0.9676	1.1570	1.2558	1.3081
300	v	1.403	1.497	1.642	0.00191	0.00306	0.00520	0.00646
	i	342.4	369.7	400.7	440.2	525.8	618.0	660.7
	s	0.8009	0.8460	0.8960	0.9569	1.0859	1.2218	1.2829
320	v	1.395	1.486	1.620	0.001848	0.00246	0.00435	0.00565
	i	342.0	369.0	399.0	435.5	469.8	594.9	645.4
	s	0.7990	0.8437	0.8922	0.9482	1.0404	1.1857	1.2575
340	v	1.388	1.475	1.601	0.001799	0.00224	0.00362	0.00494
	i	341.6	368.2	397.5	431.9	483.1	570.9	629.2
	s	0.7972	0.8413	0.8884	0.9414	1.0182	1.1483	1.2316
360	v	1.381	1.465	1.583	0.001759	0.00211	0.00302	0.00431
	i	341.3	367.6	396.2	429.0	474.9	547.9	611.7
	s	0.7956	0.8391	0.8852	0.9357	1.0042	1.1127	1.2043
380	v	1.375	1.455	1.566	0.001727	0.00201	0.00266	0.00377
	i	341.1	367.0	395.2	426.6	468.4	530.6	594.5
	s	0.7941	0.8371	0.8824	0.9309	0.9938	1.0851	1.1778
400	v	1.369	1.445	1.550	0.00170	0.00194	0.00243	0.00334
	i	340.8	366.5	394.3	424.7	464.1	518.2	578.8
	s	0.7926	0.8350	0.8797	0.9267	0.9852	1.0651	1.1534
420	v	1.363	1.436	1.535	0.00168	0.00189	0.00228	0.00301
	i	340.5	365.9	393.3	422.9	460.4	509.1	564.7
	s	0.7911	0.8330	0.8771	0.9228	0.9786	1.0501	1.1312
440	v	1.357	1.427	1.522	0.00165	0.00185	0.00217	0.00277
	i	340.3	365.3	392.3	421.3	457.3	501.9	552.7
	s	0.7896	0.8310	0.8745	0.9193	0.9724	1.0379	1.1122
460	v	1.352	1.419	1.510	0.00164	0.00181	0.00208	0.00258
	i	340.1	365.0	391.5	419.9	454.6	496.2	542.7
	s	0.7882	0.8294	0.8720	0.9160	0.9673	1.0281	1.0959
480	v	1.347	1.412	1.499	0.00162	0.00178	0.00202	0.00244
	i	339.9	364.6	390.7	418.7	452.2	491.4	534.6
	s	0.7868	0.8278	0.8698	0.9132	0.9625	1.0197	1.0824
500	v	1.343	1.406	1.489	0.00160	0.00175	0.00196	0.00232
	i	339.7	364.2	390.0	417.6	450.0	487.4	528.1
	s	0.7855	0.8262	0.8677	0.9104	0.9582	1.0125	1.0716

460°	480°	500°	520°	550°	600°	700°	t / p, kg per sqcm	
0.00934	0.01014	0.01085	0.01150	0.01240	0.01378	0.01622	v	260
713.5	735.0	754.1	771.5	795.5	832.7	901.6	i	
1.3665	1.3952	1.4207	1.4435	1.4736	1.5169	1.5908	s	
0.00832	0.00912	0.00982	0.01046	0.01133	0.01264	0.01496	v	280
703.3	726.6	746.9	765.0	790.0	828.5	898.7	i	
1.3473	1.3785	1.4050	1.4290	1.4603	1.5049	1.5804	s	
0.00743	0.00824	0.00894	0.00955	0.01040	0.01167	0.01387	v	300
692.8	718.1	739.2	758.3	784.4	824.1	895.8	i	
1.3280	1.3623	1.3897	1.4147	1.4474	1.4933	1.5705	s	
0.00665	0.00746	0.00816	0.00877	0.00959	0.01081	0.01292	v	320
682.1	709.5	731.4	751.5	778.7	819.7	892.9	i	
1.3090	1.3463	1.3749	1.4007	1.4350	1.4824	1.5610	s	
0.00595	0.00677	0.00747	0.00807	0.00807	0.01006	0.01208	v	340
670.4	700.3	723.4	744.6	773.1	815.4	890.0	i	
1.2892	1.3300	1.3602	1.3872	1.4230	1.4719	1.5520	s	
0.00533	0.00616	0.00685	0.00744	0.00824	0.00939	0.01133	v	360
657.7	690.3	715.3	737.7	767.5	811.0	887.0	i	
1.2678	1.3127	1.3455	1.3742	1.4111	1.4617	1.5433	s	
0.00479	0.00562	0.00630	0.00689	0.00767	0.00879	0.01067	v	380
644.1	679.6	707.1	730.8	761.8	806.7	884.1	i	
1.2461	1.2947	1.3310	1.3614	1.3996	1.4518	1.5351	s	
0.00431	0.00513	0.00582	0.00639	0.00716	0.00825	0.01007	v	400
630.8	668.7	698.7	723.8	756.0	802.3	881.2	i	
1.2251	1.2767	1.3166	1.3486	1.3885	1.4423	1.5271	s	
0.00390	0.00470	0.00537	0.00594	0.00670	0.00776	0.00953	v	420
617.8	658.1	690.2	716.5	750.2	797.9	878.3	i	
1.2049	1.2592	1.3022	1.3358	1.3776	1.4331	1.5193	s	
0.00354	0.00431	0.00498	0.00554	0.00628	0.00732	0.00903	v	440
605.0	647.6	681.8	709.3	744.3	793.4	875.1	i	
1.1855	1.2421	1.2878	1.3232	1.3668	1.4240	1.5118	s	
0.00325	0.00397	0.00462	0.00518	0.00590	0.00692	0.00859	v	460
592.3	637.1	673.4	702.3	738.5	789.0	872.4	i	
1.1661	1.2254	1.2738	1.3112	1.3561	1.4151	1.5046	s	
0.00302	0.00368	0.00431	0.00485	0.00556	0.00656	0.00818	v	480
581.2	626.6	665.0	695.3	727.7	784.6	869.5	i	
1.1491	1.2091	1.2598	1.2992	1.3457	1.4064	1.4976	s	
0.00282	0.00343	0.00402	0.00455	0.00524	0.00622	0.00781	v	500
572.0	616.1	656.8	688.3	726.9	780.2	866.6	i	
1.1344	1.1932	1.2464	1.2874	1.3353	1.3978	1.4907	s	

Mean Volume Heat Capacity of Gases at Constant Pressure from Spectroscopic Data (Cal per cum/deg)

°C	O_2	N_2	H_2	CO	CO_2	H_2O	Air
0	0.312	0.311	0.305	0.311	0.387	0.356	0.311
100	0.315	0.311	0.308	0.311	0.411	0.359	0.311
200	0.319	0.312	0.310	0.313	0.432	0.362	0.312
300	0.324	0.314	0.311	0.315	0.449	0.367	0.315
400	0.329	0.316	0.311	0.318	0.464	0.372	0.318
500	0.334	0.319	0.312	0.321	0.479	0.378	0.321
600	0.339	0.321	0.313	0.325	0.492	0.384	0.324
700	0.343	0.325	0.314	0.328	0.503	0.390	0.328
800	0.347	0.328	0.315	0.332	0.514	0.396	0.331
900	0.350	0.331	0.316	0.335	0.530	0.403	0.334
1 000	0.353	0.334	0.318	0.338	0.532	0.409	0.337
1 100	0.356	0.337	0.319	0.341	0.540	0.415	0.340
1 200	0.358	0.340	0.321	0.344	0.547	0.422	0.343
1 300	0.361	0.342	0.323	0.346	0.553	0.428	0.345
1 400	0.363	0.345	0.325	0.349	0.559	0.433	0.348
1 500	0.365	0.347	0.327	0.351	0.565	0.439	0.350
1 600	0.367	0.349	0.329	0.353	0.570	0.445	0.352
1 700	0.369	0.351	0.331	0.355	0.574	0.450	0.354
1 800	0.371	0.353	0.333	0.357	0.579	0.455	0.356
1 900	0.373	0.355	0.335	0.358	0.583	0.460	0.357
2 000	0.375	0.356	0.336	0.360	0.586	0.464	0.359
2 100	0.377	0.358	0.338	0.362	0.590	0.469	0.361
2 200	0.378	0.360	0.340	0.363	0.593	0.473	0.362
2 300	0.380	0.361	0.342	0.364	0.596	0.477	0.364
2 400	0.381	0.363	0.344	0.366	0.599	0.481	0.365
2 500	0.383	0.364	0.346	0.367	0.602	0.485	0.366
2 600	0.385	0.365	0.347	0.368	0.605	0.488	0.367
2 700	0.386	0.366	0.349	0.369	0.607	0.492	0.369
2 800	0.387	0.367	0.350	0.370	0.610	—	0.370
2 900	0.389	0.368	0.352	0.371	0.612	—	0.371
3 000	0.390	0.369	0.355	0.372	0.614	—	0.372

Saturated Steam (by temperatures)

t °C	p, kg per sqcm	v', cum per kg	v'', cum per kg	γ'', kg per cum	i', Cal/kg	i'', Cal/kg	r, Cal/kg	s', Cal/kg×deg	s'', Cal/kg×deg
0	0.006228	0.0010002	206.3	0.004846	0	597.2	597.2	0	2.1863
5	0.008890	0.0010000	147.2	0.006795	5.03	599.4	594.4	0.0182	2.1551
10	0.012513	0.0010004	106.4	0.009396	10.04	601.6	591.6	0.0361	2.1253
15	0.017376	0.0010010	77.99	0.01282	15.04	603.8	588.8	0.0536	2.0970
20	0.02383	0.0010018	57.84	0.01729	20.03	606.0	586.0	0.0708	2.0697
25	0.03229	0.0010030	43.41	0.02304	25.02	608.2	583.2	0.0876	2.0436
30	0.04325	0.0010044	32.93	0.03036	30.00	610.4	580.4	0.1042	2.0187
35	0.05733	0.0010061	25.25	0.03960	34.99	612.5	577.5	0.1205	1.9947
40	0.07520	0.0010079	19.55	0.05114	39.98	614.7	574.7	0.1366	1.9718
45	0.09771	0.0010099	15.28	0.06544	44.96	616.8	571.8	0.1524	1.9498
50	0.12578	0.0010121	12.05	0.08298	49.95	619.0	569.0	0.1679	1.9287
55	0.16051	0.0010145	9.584	0.1043	54.94	621.0	566.1	0.1833	1.9085
60	0.2031	0.0010171	7.682	0.1302	59.94	623.2	563.3	0.1984	1.8891
65	0.2550	0.0010199	6.206	0.1611	64.93	625.2	560.3	0.2133	1.8702
70	0.3177	0.0010228	5.049	0.1981	69.93	627.3	557.4	0.2280	1.8522
75	0.3931	0.0010258	4.136	0.2418	74.94	629.3	554.4	0.2425	1.8349
80	0.4829	0.0010290	3.410	0.2933	79.95	631.3	551.3	0.2567	1.8178
85	0.5894	0.0010323	2.830	0.3534	84.96	633.2	548.2	0.2708	1.8015
90	0.7149	0.0010359	2.361	0.4235	89.98	635.1	545.1	0.2848	1.7858
95	0.8619	0.0010396	1.981	0.5045	95.01	637.0	542.0	0.2985	1.7708
100	1.0332	0.0010435	1.673	0.5977	100.04	638.9	538.9	0.3121	1.7561
105	1.2318	0.0010474	1.419	0.7045	105.08	640.7	535.6	0.3255	1.7419
110	1.4609	0.0010515	1.210	0.8265	110.12	642.5	532.4	0.3387	1.7282
115	1.7239	0.0010558	1.036	0.9650	115.18	644.3	529.1	0.3519	1.7150
120	2.0245	0.0010603	0.8914	1.122	120.3	646.0	525.7	0.3647	1.7018
125	2.3666	0.0010650	0.7701	1.299	125.3	647.7	522.4	0.3775	1.6895
130	2.7544	0.0010697	0.6680	1.496	130.4	649.3	518.6	0.3901	1.6772
135	3.192	0.0010746	0.5817	1.719	135.5	650.8	515.3	0.4026	1.6652
140	3.685	0.0010798	0.5084	1.967	140.6	652.2	511.9	0.4150	1.6539
145	4.237	0.0010850	0.4459	2.243	145.8	654.0	508.2	0.4272	1.6428
150	4.854	0.0010906	0.3924	2.548	150.9	655.5	504.6	0.4395	1.6320
155	5.540	0.0010963	0.3464	2.887	156.1	656.9	500.8	0.4516	1.6214
160	6.302	0.0011021	0.3068	3.260	161.3	658.3	497.0	0.4637	1.6112
165	7.146	0.0011082	0.2724	3.671	166.5	659.6	493.1	0.4756	1.6012
170	8.076	0.0011144	0.2426	4.622	171.7	660.9	489.2	0.4874	1.5914
175	9.101	0.0011210	0.2166	4.617	176.9	662.1	485.2	0.4991	1.5818
180	10.225	0.0011275	0.1939	5.157	182.2	663.2	481.0	0.5107	1.5721
185	11.456	0.0011345	0.1739	5.749	187.5	664.3	476.8	0.5222	1.5629
190	12.800	0.0011415	0.1564	6.392	192.8	665.3	472.5	0.5336	1.5538
195	14.265	0.0011490	0.1410	7.094	198.1	666.2	468.1	0.5449	1.5448

Continued

t, °C	p, kg per sqcm	v', cum per kg	v'', cum per kg	γ'', kg per cum	i', Cal/kg	i'', Cal/kg	r, Cal/kg	s', Cal/kg×deg	s'', Cal/kg×deg
200	15.857	0.0011565	0.1273	7.857	203.5	667.0	463.5	0.5562	1.5358
205	17.585	0.0011645	0.1151	8.687	208.9	667.7	458.8	0.5675	1.5270
210	19.456	0.0011726	0.1043	9.585	214.3	668.3	454.0	0.5788	1.5184
215	21.477	0.0011812	0.09472	10.56	219.8	668.8	449.0	0.5899	1.5099
220	23.659	0.0011900	0.08614	11.61	225.3	669.2	443.9	0.6010	1.5012
225	26.007	0.0011991	0.07845	12.75	230.8	669.5	438.7	0.6120	1.4926
230	28.531	0.0012088	0.07153	13.98	236.4	669.7	433.3	0.6229	1.4840
235	31.239	0.0012186	0.06530	15.31	242.1	669.7	427.6	0.6339	1.4755
240	34.140	0.0012291	0.05970	16.75	247.7	669.6	421.9	0.6448	1.4669
245	37.244	0.0012400	0.05465	18.30	253.5	669.4	415.9	0.6558	1.4584
250	40.56	0.0012512	0.05006	19.98	259.2	669.0	409.8	0.6667	1.4499
255	44.10	0.0012629	0.04591	21.78	265.0	668.4	403.4	0.6776	1.4413
260	47.87	0.0012755	0.04213	23.74	271.0	667.8	396.8	0.6886	1.4327
265	51.88	0.0012888	0.03870	25.84	277.0	666.9	389.9	0.6994	1.4240
270	56.14	0.0013023	0.03557	28.11	283.0	665.9	382.9	0.7103	1.4153
275	60.66	0.0013169	0.03272	30.57	289.2	664.8	375.6	0.7212	1.4066
280	65.46	0.0013321	0.03010	33.22	295.3	663.5	368.2	0.7321	1.3978
285	70.54	0.0013484	0.02771	36.09	301.6	661.9	360.3	0.7431	1.3888
290	75.92	0.0013655	0.02552	39.18	308.0	660.2	352.2	0.7542	1.3797
295	81.60	0.0013837	0.02350	42.56	314.4	658.3	343.9	0.7653	1.3706
300	87.61	0.0014036	0.02163	46.24	321.0	656.1	335.1	0.7767	1.3613
305	93.95	0.001425	0.01991	50.22	327.7	653.6	325.9	0.7880	1.3516
310	100.64	0.001448	0.01830	54.64	334.6	650.8	316.2	0.7994	1.3415
315	107.69	0.001472	0.01682	59.46	341.7	647.8	306.1	0.8110	1.3312
320	115.13	0.001499	0.01544	64.79	349.0	644.2	295.2	0.8229	1.3206
325	122.95	0.001529	0.01415	70.68	356.5	640.4	283.9	0.8351	1.3097
330	131.18	0.001562	0.01295	77.20	364.2	636.0	271.8	0.8476	1.2982
335	139.85	0.001598	0.01183	84.55	372.3	631.1	258.8	0.8604	1.2860
340	148.96	0.001641	0.01076	92.90	380.7	625.6	244.9	0.8734	1.2728
345	158.54	0.001692	0.009759	102.4	389.6	619.3	229.7	0.8871	1.2586
350	168.63	0.001747	0.008803	113.6	398.9	611.9	213.0	0.9015	1.2433
355	179.24	0.001814	0.007875	127.0	409.5	603.2	193.7	0.9173	1.2263
360	190.42	0.001907	0.006963	143.6	420.9	592.8	171.9	0.9353	1.2072
365	202.21	0.00203	0.00606	165.0	434.2	579.6	145.4	0.9553	1.1833
370	214.68	0.00223	0.00500	200	452.3	559.3	107.0	0.9842	1.1506
374	225.2	0.00279	0.00347	288	485.3	512.7	27.4	1.03	1.08

Parameters of the Critical Point

Temperature	374.15°C
Pressure	225.65 kg per sqcm
Volume	0.00307 cum per kg

Saturated Mercury Vapour

Pressure p, kg per sqcm	Temperature of saturation, t', °C	Enthalpy		Heat of steam formation, r, Cal/kg×deg	Entropy		Specific volume	
		of the liquid, i_s, Cal/kg	of the steam, i'', Cal/kg		of the liquid s', Cal/kg×deg	of the steam s''	of the liquid v', cum per kg	of the steam v''
0.0010	119.5	3.96	76.22	72.26	0.0119	0.1959	0.0000752	165.9
0.002	134.5	4.45	76.61	72.61	0.0132	0.1902	754	86.16
0.004	151.2	4.98	77.03	72.05	0.0145	0.1843	756	44.84
0.006	161.5	5.34	77.32	71.98	0.0152	0.1808	758	30.62
0.008	168.9	5.58	77.52	71.94	0.0158	0.1785	759	23.35
0.010	175.0	5.79	77.69	71.90	0.0163	0.1767	0.0000760	18.94
0.02	195.0	6.44	78.20	71.76	0.0178	0.1711	762	9.893
0.04	216.9	7.16	78.78	71.62	0.0193	0.1654	765	5.178
0.06	230.9	7.63	79.16	71.53	0.0202	0.1621	767	3.550
0.08	241.0	7.98	79.44	71.46	0.0208	0.1598	769	2.716
0.10	249.6	8.25	79.66	71.41	0.0213	0.1580	0.0000770	2.209
0.20	277.3	9.16	80.38	71.22	0.0231	0.1525	774	1.163
0.30	294.4	9.73	80.84	71.11	0.0241	0.1494	776	0.7995
0.40	308.0	10.18	81.19	71.01	0.0249	0.1471	778	0.6140
0.5	318.8	10.55	81.49	70.94	0.0255	0.1453	0.0000780	0.5003
0.6	328.0	10.86	81.74	70.88	0.0260	0.1439	781	0.4234
0.7	335.9	11.12	81.94	70.82	0.0265	0.1428	782	0.3677
0.8	342.7	11.34	82.01	70.77	0.0269	0.1418	783	0.3253
0.9	349.2	11.56	82.29	70.73	0.0272	0.1408	784	0.2922
1.0	155.0	11.76	82.45	70.69	0.0275	0.1400	0.0000785	0.2655
1.2	365.3	12.11	82.63	70.62	0.0280	0.1386	787	0.2249
1.4	374.5	12.38	82.97	70.56	0.0285	0.1375	788	0.1953
1.6	381.9	12.64	83.14	70.50	0.0290	0.1366	789	0.1730
1.8	389.3	12.90	83.35	70.45	0.0294	0.1357	0.0000790	0.1555
2.0	395.8	13.11	83.51	70.40	0.0297	0.1349	791	0.1414
3.0	422.4	14.04	84.25	70.21	0.0309	0.1320	0.0000795	0.09789
4.0	442.4	14.75	84.80	70.06	0.0319	0.1298	798	0.07558
4.5	451.0	15.03	85.02	69.99	0.0323	0.1289	799	0.06801
5.0	458.9	15.30	85.23	69.93	0.0327	0.1282	0.0000801	0.06187
6.0	472.8	15.78	85.59	69.81	0.0334	0.1270	803	0.05254
7.0	485.1	16.20	85.91	69.71	0.0339	0.1258	805	0.04578
8.0	496.3	16.59	86.20	69.61	0.0344	0.1249	806	0.04065
9.0	506.3	16.94	86.47	69.53	0.0349	0.1241	808	0.03660
10	515.5	17.25	86.70	69.45	0.0353	0.1234	0.0000809	0.03333

Gas	Chemical formula	Atomic or molecular weight	Gas constant, R, kg-m per kg×deg	Normal specific weight γ_0, kg per cum		Temperature, °C	
				Computed	Measured	boiling point at 760 mm Hg	fusing point
Nitrogen	N_2	28.02	30.26	1.250	1.251	—195.8	—210.01
Ammonia	NH_3	17.03	49.79	0.760	0.771	—33.4	—77.7
Argon	Ar	39.94	21.26	1.782	1.784	—186.0	—189.3
Acetylene	C_2H_2	26.02	32.59	1.162	1.171	—83.6	—81
Air	—	(28.96)	29.27	1.292	1.293	—192-195	—
Hydrogen	H_2	2.016	420.6	0.0899	0.899	—252.8	—259.2
Helium	He	4.002	212.00	0.1786	0.1785	—268.95	—271.4
Nitrogen dioxide	NO_2	46.01	18.40	2.054	—	+21.2	—10.8
Diphthordichlormethane	CF_2Cl_2	120.92	7.01	5.394	5.083	—29.8	—155.0
Oxygen	O_2	32.000	26.5	1.428	1.429	—182.98	—218.74
Methane	CH_4	16.03	52.90	0.715	0.717	—161.7	—182.6
Neon	Ne	20.183	41.98	0.900	—	—246.0	—248.6
Nitrogen monoxide	NO	30.01	28.26	1.339	—	—151.0	—163.7
Carbon monoxide	CO	28.00	30.29	1.250	1.250	—191.5	—205
Propane	C_3H_8	44.06	19.25	1.967	2.019	—42.6	—189.9
Hydrogen sulphide	H_2S	34.09	24.90	1.521	—	—60.2	—83
Sulphur dioxide	SO_2	64.06	13.24	2.858	2.926	—10.0	—75.3
Carbon dioxide	CO_2	44.00	19.27	1.963	1.977	—78.5	—56
Chlorine	Cl_2	70.91	11.96	3.16	3.22	—33.95	—100.5
Ethane	C_2H_6	30.06	28.21	1.341	1.356	—88.6	—186.3
Ethylene	C_2H_4	28.03	30.25	1.251	1.261	—103.5	—169.4

The computed value of γ_0 is obtained by dividing μ by 22.416; the difference state of an ideal gas.

Characteristics of Gases

Heat, Cal/kg		Critical parameters			Heat capacity c_p at 0° C, Cal/kg×deg	$k=\frac{c_p}{c_v}$ at 0° C
of evaporation at boiling point corresponding to 760 mm Hg	of fusion	t_{cr}, °C	p_{cr}, atm	γk_{cr}, kg per cum		
47.58	6.1	−147.1	33.5	310.96	0.243	1.40
328	83.7	+132.4	111.5	236	0.492	1.32
38.9	6.7	−122.4	48.0	531	0.125	1.66
198	—	+36.0	61.7	231	0.385	1.26
47	—	−140.75-140.65	37.25-37.17	310-350	0.240	1.40
108.5	14	−239.9	12.8	31	3.394	1.41
4.66	1.365	−267.9	2.3	69.3	1.250	1.66
170.0	33.3	+158.2	100.0	570	—	—
39.9	—	+111.5	39.56	556	—	1.14
50.92	3.3	−118.8	49.7	429.9	0.219	1.40
122	14.5	−82.0	45.8	162	0.518	1.31
20.5	3.4	−228.7	25.9	483.5	—	—
106.6	18.4	−94	65	520	—	—
50.5	8.0	−138.7	34.6	311	0.249	1.40
102	19.2	+96.8	42.0	232	0.371	1.14
131	18.5	+100.4	188.9	—	0.253	1.32
94	32.2	+157.2	77.7	520	0.151	1.29
137	45.3	+31.0	72.9	460	0.196	1.30
72.95	30.1	+144.0	76	573	0.115	1.36
116	29.2	+32.1	48.8	210	0.386	1.22
115	28.5	+9.7	50.7	220	0.357	1.25

between the computed and measured values is explained by deviations from the

TABLE 1

Molar Enthalpy of Gases in the Ideal State

μi

(Cal/kmole)

t, °C \ μ	H_2 2.016	O_2 32.000	N_2 28.02	CO 28.00	CO_2 44.00	H_2O 18.016
0	0	0	0	0	0	0
100	691.7	704.9	696.1	696.8	917.2	805.9
200	1 390	1 430	1 397	1 400	1 923	1 630
300	2 090	2 178	2 106	2 115	3 005	2 477
400	2 792	2 950	2 828	2 846	4 149	3 352
500	3 497	3 741	3 567	3 595	5 344	4 255
600	4 206	4 552	4 321	4 361	6 583	5 187
700	4 922	5 375	5 092	5 140	7 857	6 151
800	5 646	6 212	5 876	5 930	9 162	7 145
900	6 380	7 058	6 673	6 738	10 493	8 170
1000	7 125	7 908	7 480	7 555	11 848	9 224
1100	7 878	8 772	8 298	8 383	13 222	10 306
1200	8 642	9 642	9 125	9 220	14 611	11 414
1300	9 417	10 514	9 962	10 070	16 013	12 546
1400	10 200	11 395	10 805	10 920	17 426	13 702
1500	11 000	12 282	11 653	11 775	18 849	14 877
1600	11 800	13 174	12 506	12 634	20 282	16 072
1700	12 610	14 074	13 362	13 496	21 724	17 287
1800	13 430	14 976	14 222	14 364	23 175	18 517
1900	14 260	15 884	15 086	15 234	24 630	19 758
2000	15 090	16 798	15 952	16 108	26 092	21 016

Note: Tables 1 and 2 have been compiled from data given by M. P. Vukalovich, V. A. Kirillin, V. N. Timofeyev and V. S. Siletsky in Справочник машиностроения, т. I., 1951 (Machinery Handbook, V. I, 1951). As applied to H_2 they are the data of mean molar heat capacity from Сборник задач по технической термодинамике (Problems in Thermodynamics) by V. A. Kirillin and A. E. Sheindlin, 1949.

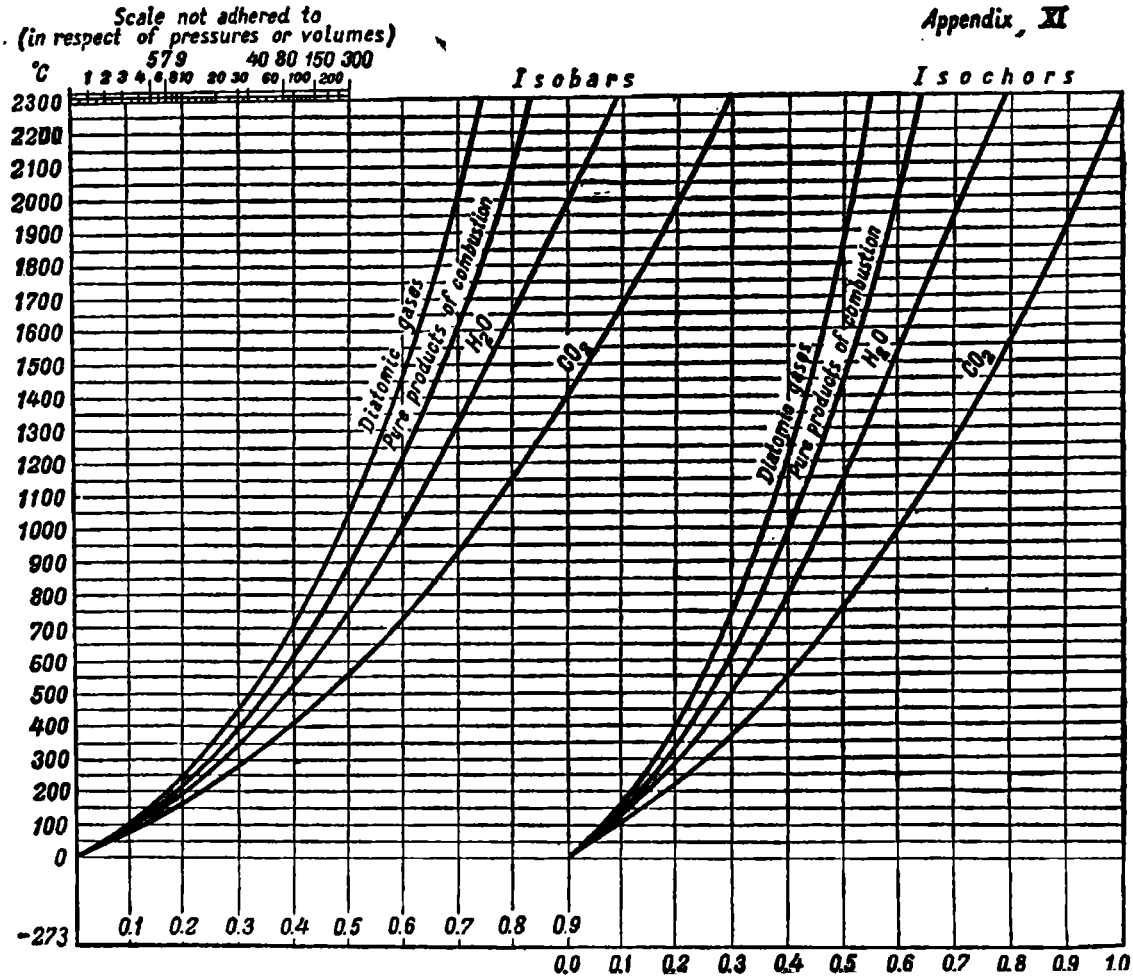
TABLE 2

Molar Internal Energy of Gases in the Ideal State

μu

(Cal/kmole)

t, °C \ μ	H_2 2.016	O_2 32.000	N_2 28.02	CO 28.00	CO_2 44.00	H_2O 18.016
0	0	0	0	0	0	0
100	493.1	506.3	497.5	498.2	718.6	607.3
200	993	1 033	1 000	1 003	1 526	1 233
300	1 494	1 583	1 510	1 519	2 439	1 882
400	1 998	2 154	2 034	2 052	3 354	2 558
500	2 504	2 746	2 574	2 602	4 351	3 262
600	3 014	3 356	3 130	3 169	5 391	3 995
700	3 532	3 986	3 702	3 750	6 467	4 761
800	4 057	4 621	4 287	4 344	7 573	5 556
900	4 593	5 268	4 885	4 951	8 706	6 383
1000	5 139	5 922	5 494	5 570	9 862	7 238
1100	5 139	6 585	6 114	6 199	11 037	8 121
1200	6 259	7 253	6 742	3 595	12 228	9 031
1300	6 835	7 934	7 380	7 488	13 432	9 965
1400	7 420	8 614	8 025	8 140	14 645	10 921
1500	8 021	9 303	8 675	8 796	15 870	11 898
1600	8 622	9 997	9 328	9 456	17 104	12 894
1700	9 234	10 698	9 986	10 120	18 348	13 911
1800	9 855	11401	10 647	10 789	19 600	14 942
1900	10 490	12 114	11 313	11 463	20 856	15 985
2000	11 120	12 826	11 980	12 136	22 120	17 044



Heat diagram *Ts* for air and the products

NOTATION

a	coefficient of proportionality (in kinetic theory)
a, b	constants in Van der Waals Equation
ata	absolute atmosphere (barometric)
atm	technical atmosphere (manometric)
c, C	heat capacity
c_p	heat capacity at constant pressure
c_v	heat capacity at constant volume
c_m	mean heat capacity
c	velocity of stream
c_{cr}	critical velocity
C	Centigrade scale of thermometer
Cal	Calorie, great calorie
Cal p. h.	Calories per hour
Cal/kg	Calories per kilogram
Cal p. m.	Calories per minute
const	constant value
cucm	cubic centimetres
cum	cubic metres
cum-kg	cubic metres per kg
d	moisture content of damp air
d_t	specific consumption of steam
f	function
F, f	area
G, g	weight in kilograms
h	specific work
h	adiabatic heat drop
h. p.	horse power
hp-hr	horse-power-hour
I, i	enthalpy (heat content)
i	degrees of freedom (in kinetic theory)
ir	irreversible (in subscripts)
K	Kelvin (absolute) thermometer scale
k	Boltzmann constant
kg	kilogram
kg-cucm	kilograms per cubic centimetre
kg-cum	kilograms per cubic metre
kg-hp-hr	kilograms per horse-power-hour
kg/hr	kilograms per hour
kg/sec	kilograms per second
kgm	kilogram-metres (unit of work)
kgm/kg	kilogram-metres per kilogram (of the working body)
kgm/sec	kilogram-metres per second
ksm	kilograms per square metre (pressure)

kw	kilowatts
kwh	kilowatt hours
L, l	work performed
l_0	available work (of stream)
LDC	left dead centre
L_w	useful work of a system
m	mass
m	subtangent to a polytrope
max	maximum (subscript)
min	minimum (subscript)
mm Hg	millimetres of a mercury column
m/sec	metres per second
n	constant polytrope exponent
p	pressure, specific
P	pressure, partial
P	probability
p_{cr}	critical pressure
Q, q	amount of heat
r	heat of steam formation
R	universal gas constant
RDC	right dead centre
rv	reversible (subscript)
S, s	entropy
STP	standard temperature and pressure (760 mm Hg at 0° C)
T	absolute temperature
t	centigrade temperature
t_{cr}	critical temperature
t_{inv}	temperature of inversion
t_s	temperature of saturation (boiling point)
U, u	internal energy
v	specific volume
V	partial volume
V_μ	volume of one mole
x	quality of steam
W_t	specific consumption of heat
α	coefficient of expansion
β	coefficient of compressibility
γ	specific weight
δ	adiabatic expansion ratio
Δ	change
ε	adiabatic compression ratio
ζ	coefficient of energy losses in nozzle
λ	pressure ratio
λ	full heat of dry saturated vapour
μ	molecular weight
η	efficiency
ρ	isobaric expansion ratio
ρ	work of dissipation
τ	period of time
φ	function
φ	velocity coefficient of nozzle
φ	relative moisture of damp air
ψ	work of expansion
$\oint$	integral of the cycle